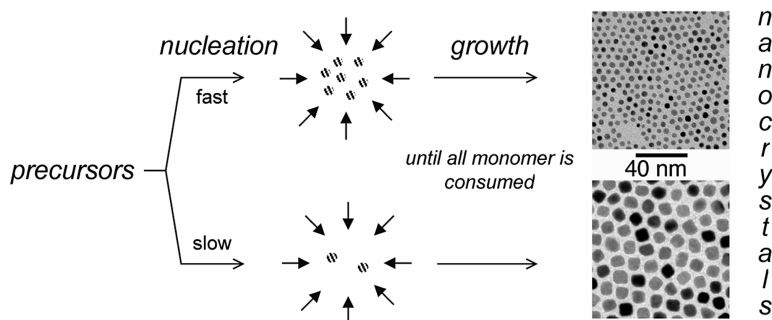


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J. Am. Chem. Soc., **2003**, 125 (30), 9090-9101 • DOI: 10.1021/ja0299371 • Publication Date (Web): 02 July 2003

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Study of Nucleation and Growth in the Organometallic Synthesis of Magnetic Alloy Nanocrystals: The Role of Nucleation Rate in Size Control of CoPt₃ Nanocrystals

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Received December 27, 2002

Abstract: High quality CoPt₃ nanocrystals were synthesized via simultaneous reduction of platinum acetylacetonate and thermodecomposition of cobalt carbonyl in the presence of 1-adamantanecarboxylic acid and hexadecylamine as stabilizing agents. The high flexibility and reproducibility of the synthesis allows us to consider CoPt₃ nanocrystals as a model system for the hot organometallic synthesis of metal nanoparticles. Different experimental conditions (reaction temperature, concentration of stabilizing agents, ratio between cobalt and platinum precursors, etc.) have been investigated to reveal the processes governing the formation of the metal alloy nanocrystals. It was found that CoPt₃ nanocrystals nucleate and grow up to their final size at an early stage of the synthesis with no Ostwald ripening observed upon further heating. In this case, the nanocrystal size can be controlled only via proper balance between the rates for nucleation and for growth from the molecular precursors. Thus, the size of CoPt₃ nanocrystals can be precisely tuned from ~3 nm up to ~18 nm in a predictable and reproducible way. The mechanism of homogeneous nucleation, evolution of the nanocrystal ensemble in the absence of Ostwald ripening, nanocrystal faceting, and size-dependent magnetic properties are investigated and discussed on the example of CoPt₃ magnetic alloy nanocrystals. The developed approach was found to be applicable to other systems, e.g., FePt and CoPd₂ magnetic alloy nanocrystals.

Introduction

Structural, magnetic, electronic, and catalytic properties of many materials are strongly size-dependent in the nanometer size scale.^{1–4} Preparation of high quality nanocrystals of a desired size is a prerequisite to investigate and utilize their size-determined properties; therefore, relatively simple and reproducible approaches for the synthesis of crystalline nanoparticles of controllable size are of great fundamental and technological interest. The synthesis of metal colloids has been studied for more than one century, but yet the number of preparations yielding a size series of monodisperse metal nanocrystals is surprisingly small.⁴ The control of the nanocrystal size and monodispersity is a key in the formation of two- or three-dimensional self-assembled structures where individual nanocrystals play the role of building blocks—artificial atoms in the next level of material hierarchy.^{4–7} During the past decade,

plenty of wet colloidal syntheses of metal nanoparticles were reported. Well-separated and nearly monodisperse gold,^{8,9} platinum,^{10,11} and silver^{12,13} nanocrystals can be prepared at room temperature by reducing the corresponding metal salt in aqueous solution or via the two-phase reduction method described by Brust et al.¹⁴ On the other hand, the synthesis of high quality transition metal nanocrystals requires other approaches because these particles do not crystallize well at room temperature.⁴ Significant progress in the preparation of transition metal nanocrystals was achieved during the last years by introducing “hot” organometallic synthetic routes where nanocrystals nucleate and grow at ~150–300°C in high-boiling solvents. Such

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- (1) Alivisatos, A. P. *Science* **1996**, *271*, 933.
- (2) Shi, J.; Gider, S.; Babcock, K.; Awschalom, D. D. *Science* **1996**, *271*, 937.
- (3) Leslie-Pelecky, D. L.; Rieke, R. D. *Chem. Mater.* **1996**, *8*, 1770.
- (4) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.

- (5) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.
- (6) Rogach, A. L.; Talapin, D. V.; Shevchenko, E. V.; Kornowski, A.; Haase M.; Weller H. *Adv. Funct. Mater.* **2002**, *12*, 653.
- (7) Collier, C. P.; Vossmeier, T.; Heath, J. R. *Annu. Rev. Phys. Chem.* **1998**, *49*, 371.
- (8) Stoeva, S.; Klabunde, K. J.; Sorensen, C. M.; Dragieva I. *J. Am. Chem. Soc.* **2002**, *124*, 2305.
- (9) Brown L. O.; Hutchison J. E. *J. Am. Chem. Soc.* **1999**, *121*, 882.
- (10) Teranishi, T.; Hosoe, M.; Tanaka, T.; Miyake, M. *J. Phys. Chem. B* **1999**, *103*, 3818.
- (11) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein A.; El-Sayed, M. A. *Science* **1996**, *272*, 924.
- (12) Korgel, B. A.; Fullam, S.; Connolly, S.; Fitzmaurice, D. *J. Phys. Chem. B* **1998**, *102*, 8379.
- (13) Murphy, C. J.; Jana, N. R. *Adv. Mater.* **2002**, *14*, 80.
- (14) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.

recipes were developed for iron,^{15,16} cobalt,^{17–19} nickel,¹⁶ and alloy FePt,²⁰ and CoPt₃²¹ nanocrystals. Monodisperse nanocrystals of magnetic materials (Fe, Co, Ni, FePt, CoPt₃, etc.) attract special attention because of their potential in ultrahigh-density magnetic data storage devices. Co–Pt alloy films have a strong perpendicular magnetic anisotropy²² and high chemical stability,²³ these alloys might also be used for magneto-optical storage media.²²

In the case of crystalline particles consisting of $\sim 10^2$ – 10^4 atoms, a nearly continuous tunability of the particle size is possible, as an addition or removal of a unit cell requires only a small variation of the nanocrystal free energy.⁶ However, in the majority of the existing routes for metal nanocrystals, tuning of the particle size is based on nearly empirical variation of the ratio between capping groups and metal precursors or on the nature of capping ligands, whereas an exact adjustment of the particle size could only be achieved via costly post-preparative size fractionation.⁴ Moreover, the mechanisms responsible for size-control at room temperature and “hot” synthetic routes are, probably, different. For instance, the room-temperature syntheses of Au and Ag nanocrystals agree with the concept of “thermodynamic size-control”—the increase of the stabilizer-to-precursor ratio results in a decrease of the particle size.²⁴ By contrast, the synthesis of Fe nanocrystals in oleic acid–dioctyl ether mixture at 300 °C revealed the opposite behavior—the nanocrystal size increases with increasing concentration of the stabilizing agent (oleic acid).²⁵ The lack of information on the processes occurring in the reaction vessel during “hot” organometallic synthesis hinders the development of predictable size-control schemes.

In this contribution, we show that size control in the “hot” synthesis of metal nanoparticles is a kinetically driven process where the ratio between the rates for nucleation and for growth is responsible for the final nanocrystal size. The control of this ratio allows an easy tuning of the nanocrystal size as demonstrated on the example of magnetic alloy CoPt₃ nanocrystals. This approach can be applied to FePt nanocrystals which are considered as promising candidates for application in ultrahigh-density magnetic storage media. To the best of our knowledge, this is the first attempt of a systematic experimental study of the “hot” synthesis of metal nanocrystals and the nucleation mechanism of metal alloy colloids.

Experimental Section

Chemicals and Apparatus. Toluene, propanol-2, *n*-hexane (Aldrich), diphenyl ether (99%, Alfa Aesar), 1,2-hexadecandiol (90%, Fluka or Lancaster), 1-adamantanecarboxylic acid (99%, Fluka, further referred to as ACA), 1,2-dichlorobenzene (99%, Acros Organics), cobalt carbonyl (Co₂(CO)₈, stabilized with 1–5% of hexane, Strem) and platinum(II)-acetylacetonate (98%, Strem, further referred to as Pt-(acac)₂) were used as received. Hexadecylamine (further referred to as HDA) (Merck) was purified by a vacuum distillation.

Powder X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), small-angle X-ray scattering (SAXS), and inductively coupled plasma atomic emission spectroscopy (ICP AES) techniques were applied to characterize the composition, structure, and size of synthesized nanocrystals. Powder XRD measurements were performed on the Philips X'Pert PRO X-ray diffraction system. Samples for XRD measurements were prepared by dropping colloidal suspension of nanocrystals in toluene on a standard single-crystal Si support and by evaporating the solvent. TEM and HRTEM images were obtained using a Philips CM-300 microscope operating at 300 kV. Samples for these measurements were prepared by depositing a drop of nanocrystal solution in toluene or hexane on carbon-coated copper grids. The excess of solvent was wicked away with a filter paper, and the grids were dried in air. Small-angle X-ray scattering (SAXS) was conducted with a modified Kratky compact camera equipped with an imaging-plate detector system (Fuji BAS MS 2525 obtained from Raytest GmbH in Straubenhardt/Germany). The light source was a standard X-ray tube with a fixed copper target operating at 40 mA and 30 kV. The light was monochromatized (wavelength = 0.1542 nm) by using a Goebel mirror from Bruker AXS. The scattering functions were transformed into size-distribution functions using an updated version of program ORT²⁶ that allows for the desmearing of slit-width and slit-length broadening as described by Glatter.^{27,28} The elemental composition of the nanocrystals was estimated either by ICP AES of the solution obtained after digesting of the particles in HCl/HNO₃ mixture or by energy-dispersive X-ray spectroscopy (EDX) of a monolayer of properly washed nanocrystals. Magnetic measurements were performed in a Quantum Design MPMS2 Superconducting Quantum Interference Device (SQUID) magnetometer.

Synthesis of CoPt₃ Nanocrystals. CoPt₃ nanocrystals were synthesized as described in Ref. [21] in a high-boiling coordinating solvent mixture (hexadecylamine–diphenyl ether). The synthesis was carried out using standard Schlenk line technique under dry argon.

In a typical synthesis, relevant amounts of 1,2-hexadecandiol (0.13 g, 0.5 mmol), Pt(acac)₂ (0.0328 g, 0.083 mmol) and 1-adamantanecarboxylic acid (0.25 g, 1.4 mmol) were dissolved in a mixture of 4 g HDA and 2 mL of diphenyl ether and heated to 65 °C in a three-neck flask until a clear solution was formed. Then, the solution was heated to a certain temperature in the range from 140 °C to 220 °C and the cobalt stock solution was swiftly injected into the hot reaction mixture under vigorous stirring. Note that the volume of the cobalt stock solution is much smaller than the total volume of the reaction mixture and injection does not considerably change the temperature of the reaction mixture. Therefore, the temperature of injection of the stock solution will be further referred to as “reaction temperature”. After injection the color changes from pale yellowish to black indicating the formation of CoPt₃ nanocrystals. Further heating usually continued for 1 h at the injection temperature and was followed by annealing at refluxing temperature (~ 275 – 285 °C) for 1 h.

The cobalt stock solution has to be freshly prepared before the synthesis by dissolving 0.043 g (0.125 mmol, a typical recipe, all other cases are summarized in Table S1 from the Supporting Information) of Co₂(CO)₈ in 0.6–0.7 mL of 1,2-dichlorobenzene at ~ 35 °C under airless conditions.

- (15) Park, S.-J.; Kim, S.; Lee, S.; Khim, Z. G.; Char, K.; Hyeon, T. *J. Am. Chem. Soc.* **2000**, *122*, 8581.
- (16) Murray, C. B.; Sun, S.; Doyle, H.; Betley, T. *MRS Bulletin* **2001**, 985.
- (17) Sun, S.; Murray, C. B.; Doyle, H. *Mater. Res. Soc. Symp. Proc.* **1999**, *577*, 385.
- (18) Sun, S.; Murray, C. B. *J. Appl. Phys.* **1999**, *85*, 4325.
- (19) Puentes, V. F.; Krishan, K. M.; Alivisatos, A. P. *Science* **2001**, *291*, 2115.
- (20) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989.
- (21) Shevchenko, E. V.; Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *J. Am. Chem. Soc.* **2002**, *124*, 11 480.
- (22) Grange, W.; Maret, M.; Kappler, J.-P.; Vogel, J.; Fontaine, A.; Petroff, F.; Krill, G.; Rogalev, A.; Coulon, J.; Finazzi, M.; Brookes, N. *Phys. Rev. B* **1998**, *58*, 6298. (b) Weller, D.; Brändle, H.; Gorman, G.; Lin, C.-J.; Notarys, H. *Appl. Phys. Lett.* **1992**, *61*, 2726. (c) Lin, C.-J.; Gorman, G. L. *Appl. Phys. Lett.* **1992**, *61*, 1600. (d) Shapiro, A. L.; Rooney, P. W.; Tran, M. Q.; Hellman, F.; Ring, K. M.; Kavanagh, K. L.; Rellinghaus, B.; Weller, D. *Phys. Rev. B* **1999**, *60*, 12826. (e) Chang, G.; Lee, Y.; Rhee, J.; Lee, J.; Jeong, K.; Whang, C. *Phys. Rev. Lett.* **2001**, *87*, 067208–1.
- (23) Tyson, T. A.; Conradson, S. D.; Farrow, R. F. C.; Jones, B. A. *Phys. Rev. B* **1996**, *54*, R3702.
- (24) Leff, D. V.; Ohara, P. C.; Heath, J. R.; Gelbart, W. M. *J. Phys. Chem.* **1995**, *99*, 7036.
- (25) Hyeon, T.; Lee, S. S.; Park, J.; Chung, Y.; Na, H. B. *J. Am. Chem. Soc.* **2001**, *123*, 12798.

(26) Schnablegger H.; *Appl. Optics* **1991**, *30*, 4889.

(27) Glatter, O. J. *Appl. Crystallogr.* **1977**, *10*, 415.

(28) Glatter, O. J. *Appl. Crystallogr.* **1980**, *13*, 7.

We varied both the injection temperature of the cobalt stock solution and the initial concentrations of ACA, Pt(acac)₂, and Co₂(CO)₈ to investigate systematically the parameters affecting the synthesis of CoPt₃ nanocrystals. The molar ratio of 1,2-hexadecandiol to Pt(acac)₂ was always kept as 6 to 1.

The detailed conditions for the preparation of colloidal CoPt₃ nanocrystals ranging from ~3 to 18 nm are summarized in Table S1 in the Supporting Information and are discussed in more detail in the Results and Discussion sections. The nanocrystal sizes were perfectly reproduced from run to run (within ~10% error bar).

Post-Preparative Procedures. After cooling the reaction mixture to 50°C all subsequent steps were performed in air. The crude solution of CoPt₃ nanoparticles was mixed with ~5 mL of chloroform. Subsequently, 20 mL of propanol-2 were added, resulting in a black precipitate which was isolated by centrifugation. The precipitate was redissolved in toluene (~5 mL) and filtered through a 0.2 μm PTFE filter. To wash out the excess of stabilizers, the nanocrystals were precipitated again by addition of ~20 mL of propanol-2 and centrifuged. The resulting black precipitate containing CoPt₃ nanocrystals can be redissolved in various nonpolar solvents (toluene, hexane, chloroform, etc.). A small amount (~0.1 mg) of HDA can be added to the solution of the nanocrystals to improve their solubility and the stability of the colloidal solution. No further size selection was applied.

Results

General Remarks on the Synthesis and Characterization of CoPt₃ Nanocrystals. CoPt₃ nanocrystals were prepared via the simultaneous reduction of Pt(acac)₂ and thermal decomposition of Co₂(CO)₈ in the presence of 1-adamantanecarboxylic acid (ACA) and hexadecylamine (HDA) as stabilizing agents. This synthetic approach has been introduced by us in Ref. [21] and is described in the Experimental Section. Synthesized nanocrystals were routinely investigated by powder-XRD and TEM measurements in order to collect statistically reliable data about the dependence of the nanocrystal size, shape, and crystallinity on various reaction parameters. Nanocrystal sizes estimated by these methods will be further referred to as “XRD-size” and “TEM-size” correspondingly. The width of the XRD peaks provides information about the X-ray coherence length which is close to the average size of the single crystalline domain inside the nanocrystal. Figure 1 shows the systematic evolution of XRD patterns of chemically disordered *fcc* phase CoPt₃ nanocrystals upon increase of their size from ~3 to 17 nm. All samples were synthesized in form of stable colloidal solutions via the same chemical route applying the nanocrystal size-control techniques described below. CoPt₃ nanocrystals larger than ~13 nm are stable in crude solutions only at temperatures above ~100 °C because of their strong magnetic dipole interactions which result in nanocrystal aggregation at room temperature.

It was found that different experimental conditions (reaction temperature, ratio between the cobalt and platinum precursors, etc.) yielded nanocrystals with identical chemical composition. Both EDX measurements and chemical analysis of digested nanocrystals indicated compositions being very close to the ratio given by the CoPt₃ formula.

Injection of the cobalt stock solution results in a color change of the reaction mixture from pale yellowish to black. The temporal evolution of the absorption spectra of crude solutions is shown in the Supporting Information. If the injection temperature is higher than ~170 °C or if the injection is followed by fast heating of the crude solution to the boiling point, then the particles rapidly nucleate and grow up to their

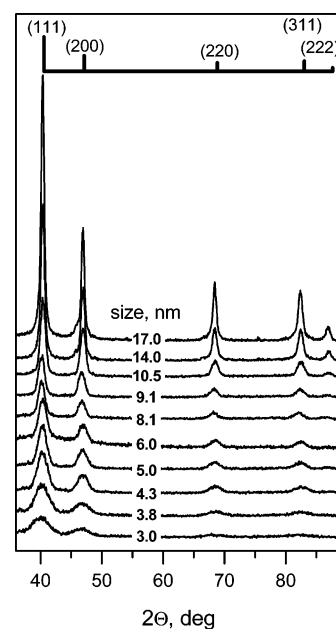


Figure 1. Size-dependent powder-XRD patterns of CoPt₃ nanocrystals. The average nanocrystal sizes were calculated by the Debye-Scherrer equation. Reflexes of bulk *fcc* CoPt₃ phase are shown with a stick spectrum.

final size (Figure 2a). Subsequent heating does not result in any detectable changes of the particle size (Figure 2a). Thus, no Ostwald ripening was observed for CoPt₃ nanocrystals. Prolonged excessive refluxing (days) led to the progressive decomposition of organics rather than to particle growth. The chemical analysis of the solution remaining after precipitation of the nanocrystals shows that all Pt(acac)₂ is converted to nanocrystals during the first several minutes after starting the process. Note that we always used some excess of the cobalt precursor (see the Experimental Section). Moreover, no change of the absorption spectra of the crude solution was observed at late stages of the nanocrystal synthesis (Figure S1, Supporting Information). Therefore, we can conclude that no changes of the particle concentration takes place at late stages of the reaction. Summarizing, at high reaction temperature all CoPt₃ nanocrystals form immediately after injection of the cobalt crude solution, rapidly growing and reaching some size which cannot be changed by further heat treatment. In the case of a lower reaction temperature, e.g., 145°C, the nanocrystals nucleate during ~2 min after the injection of cobalt stock solution and grow during ~10 min as evidenced from measurements of the TEM-size (Figure 2b). Below 130°C no formation of CoPt₃ nanocrystals was observed in a reasonable time window.

More detailed analysis of the temporal evolution of CoPt₃ nanocrystals in the reaction mixture shows a large difference between XRD and TEM sizes (Figure 2b) for samples taken directly after the formation of the particles. Annealing of the CoPt₃ nanocrystals at the boiling point (~275–285 °C) of the crude solution for ~30 min results in an increase of the XRD-size but no considerable changes of the TEM-size are observed (Figure 2b). The XRD-size (X-ray coherence length) is considerably smaller than the whole nanocrystal probably due to some defects of the crystalline lattice.²⁹ We believe that the observed decrease of the difference between XRD- and TEM-

(29) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.

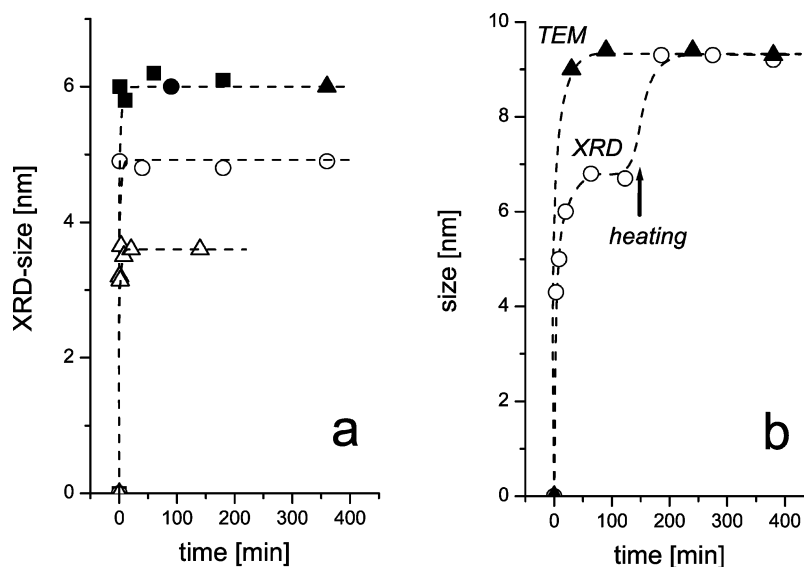


Figure 2. (a) Dependence of CoPt₃ nanocrystals size on duration of heating. After injection of the cobalt stock solution at 100 °C, the reaction mixture was rapidly (~ 22 °C/min) heated to ~ 275 °C. The molar ratios of Pt: Co: ACA were 1:3:2 (○) and 1:3:6 (●, ■, ▲—indicates three different preparations). The evolution of the nanocrystal size during the reaction carried out by injection and heating at 200 °C is shown by (Δ) (b) Evolution of the XRD (○) and TEM (▲) sizes of CoPt₃ nanocrystals upon formation and annealing. The injection temperature of the cobalt stock solution is 145 °C. Molar ratio Pt: Co: ACA is 1:3:6. Arrow corresponds to the increase of the reaction temperature from 145 °C to ~ 275 °C.

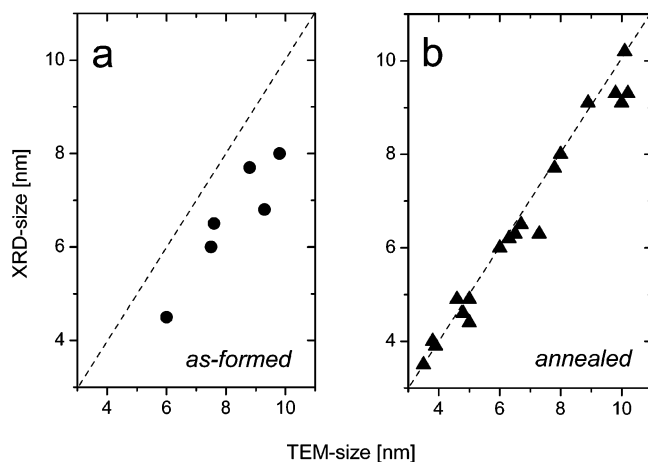


Figure 3. Comparison of the XRD- and TEM-sizes before and after annealing showing the influence of the annealing procedure on the crystallinity of CoPt₃ nanoparticles.

sizes is a result of the annealing of defects²⁹ accompanied by an improvement of the particle crystallinity. This annealing process requires relatively high temperatures (200–300 °C) necessary to trigger atom diffusion inside the nanocrystals.³⁰ A more detailed description of the temporal evolution of the CoPt₃ nanocrystal size upon annealing is given in Figure S2 from the Supporting Information.

An improvement of the particle crystallinity has been observed for all nanocrystal sizes (Figure 3). It allowed us to conclude that the annealing of the crystal lattice is an important prerequisite to the formation of high-quality CoPt₃ nanocrystals. After annealing the XRD-size is nearly equal to the TEM-size (Figure 3b), indicating that most of the nanocrystals are single crystalline with nearly perfect lattice. HRTEM investigations also confirm the excellent crystallinity of annealed CoPt₃ nanocrystals (Figure 4 and Figure S3 from the Supporting Information). Nanocrystals are well separated on TEM grid and

exhibit lattice fringes without stacking faults. CoPt₃ nanocrystals larger than ~ 7 nm usually exhibit facets at cubic shape. As-prepared CoPt₃ nanocrystals have, owing to their monodispersity, a strong tendency to form self-assembled superstructures during evaporation of the solvent. Using the technique of controlled oversaturation of a colloidal solution,^{31,32} perfectly faceted macroscopic (20–50 μm) colloidal crystals consisting of CoPt₃ nanocrystals as building blocks, can be routinely grown. Figure 5 shows a HRSEM image demonstrating the ordering of ~ 6.3 nm CoPt₃ nanocrystals onto the surface of such a colloidal crystal.

To better understand the processes of formation and growth of CoPt₃ nanocrystals, we investigated the influence of the experimental conditions on the properties of the nanocrystals formed.

Effect of the Reaction Temperature (Temperature of Injection of the Co Stock Solution). In the presence of hexadecanediol the solution of Pt(acac)₂ in the HDA-ACA mixture is stable over a wide region of temperatures and starts to decompose only above ~ 220 °C. However, injection of the Co₂(CO)₈ stock solution initiates a reduction of Pt(acac)₂ already above ~ 130 °C. Formation and growth of CoPt₃ nanocrystals was investigated at different temperatures. Figure 6a shows how the final size of the CoPt₃ nanocrystal depends on the reaction temperature. An increase of the temperature from 145 °C to 220 °C allows to decrease the average final size from ~ 10 nm to 3 nm, i.e., permits the preparation of nanocrystals in a wide range of sizes. Subsequent annealing of the nanocrystals at 275–285 °C results in perfectly crystalline particles with nearly identical TEM and XRD sizes.

Effect of the Concentration of the Stabilizing Agent (1-Adamantanecarboxylic Acid). We systematically tested phos-

(30) Yang, M. H.; Flynn, C. P. *Phys. Rev. Lett.* **1989**, *62*, 2476.

(31) Talapin, D. V.; Shevchenko, E. V.; Kornowski, A.; Gaponik, N.; Haase, M.; Rogach, A. L.; Weller, H. *Adv. Mater.* **2001**, *13*, 1868.
(32) Shevchenko, E. V.; Talapin, D. V.; Kornowski, A.; Wiekhorst, F.; Kötzer, J.; Haase, M.; Rogach, A. L.; Weller, H. *Adv. Mater.* **2002**, *14*, 287.

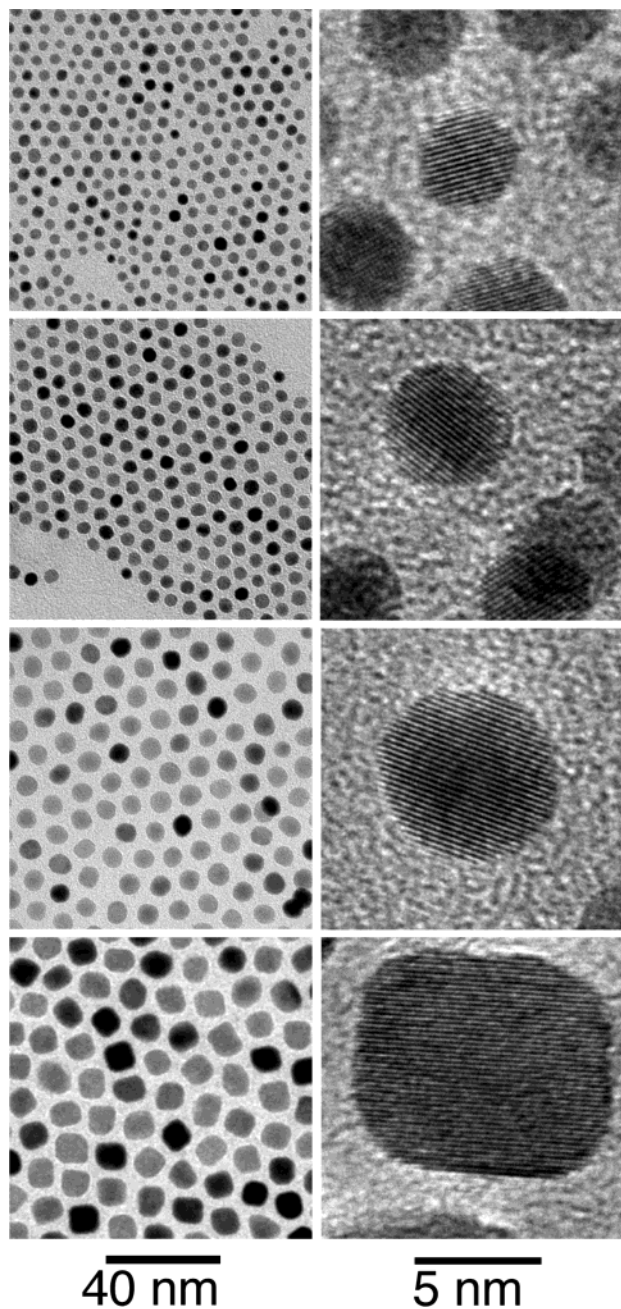


Figure 4. TEM and HRTEM images showing the effect of the reaction temperature on the mean size and size distribution of 3.7, 4.9, 6.3, and 9.3 nm CoPt₃ nanocrystals prepared at 220, 200, 170, and 145 °C and annealed at ~280 °C for 1 h. Molar ratio of Pt: Co: ACA is 1:3:6 for all samples.

phines, phosphine oxides, phosphonic acids, primary and secondary amines, fatty acids, and mixtures of these compounds as stabilizing agents for the preparation of Co–Pt alloy nanocrystals.²¹ High quality CoPt₃ nanocrystals were synthesized only in the presence of ACA or 1-adamantaneacetic acid. The unique role of these extremely bulky stabilizers in the synthesis of CoPt₃ nanocrystals was discussed in ref 21. The presence of carboxylic acid groups of ACA on the surface of nanocrystals has been proven by FTIR.²¹ In principle, CoPt₃ nanocrystals can be prepared in the presence of ACA only; however, the addition of a cosurfactant like HDA or tetradecylphosphonic acid to the reaction mixture improves the particle size distribution and stability of the colloidal solutions against aggrega-

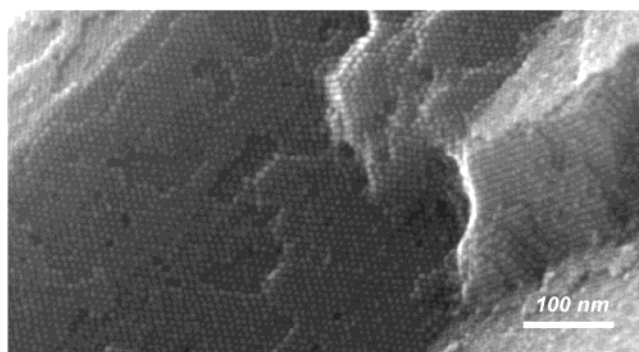


Figure 5. Monodisperse CoPt₃ nanocrystals can be used as “building blocks” to form highly ordered self-assembled superlattices.

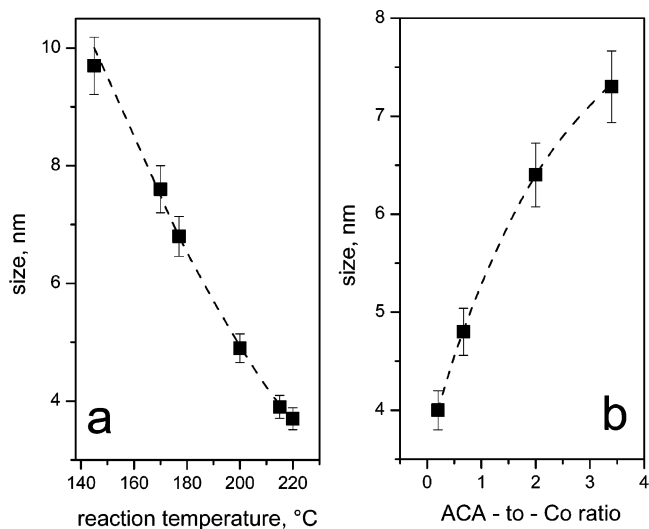


Figure 6. (a) Dependence of CoPt₃ nanocrystals size on the reaction temperature. Molar ratio of Pt:Co:ACA is 1:3:6; (b) Influence of initial amount of the stabilizing agent (ACA) on the nanocrystals size.

tion.²¹ The conventional technique for investigating the composition of the stabilizing shell is based on gentle digesting of nanocrystals with HCl/HNO₃ followed by isolation and analysis of capping ligands.³³ Unfortunately, this approach cannot be applied to CoPt₃ nanocrystals due to their high chemical stability. Digesting of the nanocrystals with HCl/HNO₃ is accompanied by oxidation of the capping ligands making the quantitative analysis of the ratio between HDA and ACA on the surface of CoPt₃ nanocrystals extremely difficult.

However, the major influence of ACA on the formation and stabilization of CoPt₃ nanocrystals is evident from the drastic influence of the initial ACA concentration on the nanocrystal size. An increase of the initial concentration of ACA results in an increase of the average nanocrystal size (Figure 6b). Thus, a variation of the concentration of ACA in the crude solution provides an easy and efficient way to control the size of CoPt₃ nanocrystals.

Effect of the Ratio between Co and Pt Precursor. In the next series of experiments, we varied the initial concentrations of Co and Pt precursors and kept both the reaction temperature and the concentrations of HDA and ACA constant. As already mentioned above, a variation of the ratio between Co and Pt precursors does not change the composition of the nanocrystals.

(33) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 3343.

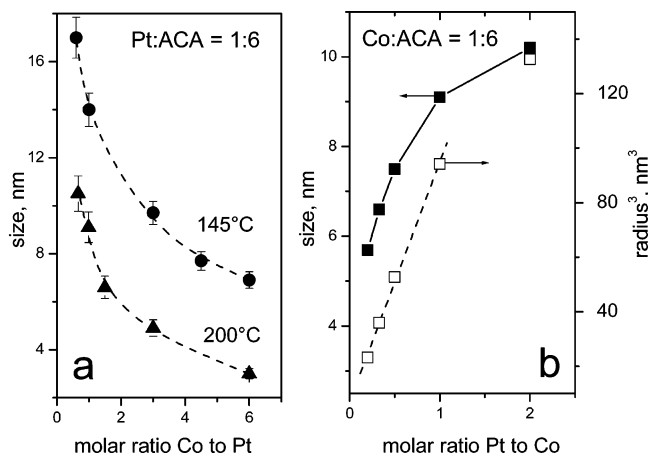


Figure 7. (a) Influence of the molar ratio between Co and Pt precursors on the nanocrystal size at different reaction temperatures. (b) Influence of the molar ratio between Pt and Co precursors on the nanocrystal size for the reaction temperature 200 °C (●) and the same data plotted in the coordinates of cube of the particle radius vs initial ratio of Pt to Co precursors (□). After the nanocrystal formation all samples were annealed at ~ 270 – 280 °C for ~ 1 h. The amount of ACA was constant (0.25 g) for all experiments.

For all nanocrystal samples a Co-to-Pt ratio very close to 1:3 was observed.

In the reaction, we always used some excess of the Co-precursor (with respect to the 1-to-3 ratio in CoPt₃ phase) to prevent the formation of bulk Pt (see the Experimental Section and ref 21). Quantitative description of all processes occurring inside the reaction vessel during the nucleation and growth of CoPt₃ nanocrystals can be rather complex. Note that both, Co and Pt precursors, compete for the finite amount of ACA and that both can be present in solution in different molecular forms. Therefore, to investigate the influence of the precursor ratio on the synthesis of CoPt₃ nanocrystals, we performed two series of experiments. In the first one, we varied the initial concentration of the Co-precursor whereas temperature and amounts of all other components were kept constant. In the second series of experiments, we varied in the same manner the initial concentration of the Pt-precursor.

An increase of the concentration of cobalt (or an increase of the Co-to-Pt ratio) in the reaction mixture resulted in a decrease of the particle size (Figure 7a). A similar behavior was observed for different reaction temperatures allowing us to tune the mean particle size from ~ 3 to 18 nm. Similarly, an increase of concentration of the Pt precursor results in an increase of the size of CoPt₃ nanocrystals (Figure 7b).

Size Distribution of the CoPt₃ Nanocrystals in Growth.

We studied the size distribution of CoPt₃ nanocrystals grown in the HDA–ACA mixture. Information about particle size distribution was obtained from statistical evaluation of all nanocrystals in a chosen area of a TEM micrograph (~ 1500 – 2000 particles) or from small-angle X-ray scattering (SAXS) data by means of the indirect transformation method.^{27,28} The latter averages over a huge number of nanocrystals whereas processing of the TEM images requires some care to avoid artifacts due to possible spatial separation of differently sized particles on the TEM grid. Figure 8a shows SAXS patterns for two samples of as-prepared CoPt₃ nanocrystals with mean sizes between ~ 4 and 10 nm. The nanocrystal size was adjusted by proper choice of the reaction temperature (215 °C and 145 °C). Figure 8, parts b and c, shows the particle size distribution functions of as-prepared ~ 4 nm CoPt₃ nanocrystals as obtained from the SAXS and TEM data, correspondingly. The SAXS data evidence that small CoPt₃ nanocrystals form stable suspensions with single-particle population.^{12,34} Both SAXS and TEM measurements confirm relatively narrow and nearly symmetric particle size distribution for as-prepared ~ 4 nm CoPt₃ nanocrystals (Figure 8, parts b and c) whereas a minor deviation between mean sizes estimated by these methods was observed. HRTEM always provided smaller estimates for particle size compared to SAXS, because the size distribution from SAXS is a volume (or mass) distribution, whereas that from microscopy is a number distribution. The difference between volume and number distribution is negligible when the distribution is narrow. However, in broad distributions or in the presence of a few aggregates the bigger particles count visibly more in volume distributions (SAXS) than in number distributions (TEM). Also note that the nanocrystal capping molecules ACA and HDA

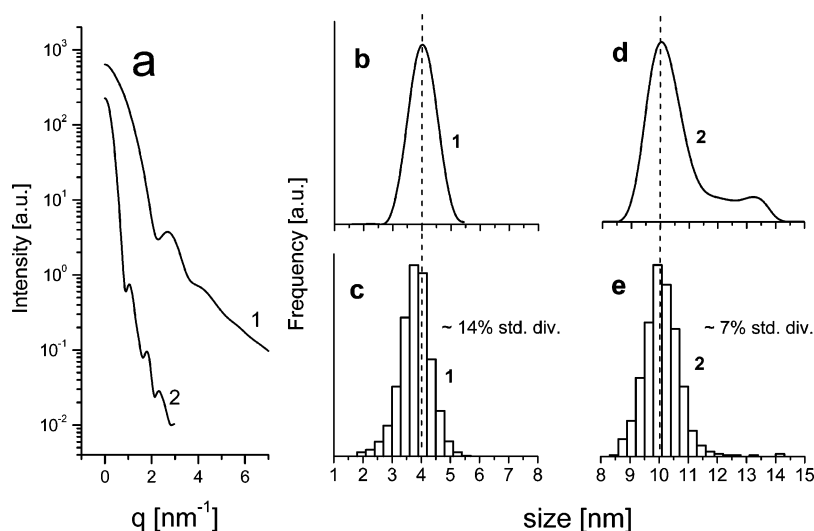


Figure 8. (a) The angular dependence of scattered X-ray intensity (SAXS) from two samples of as-prepared CoPt₃ nanocrystals with mean size (1) ~ 4 nm and (2) ~ 10 nm. (b) and (d) Particle volume fraction vs size curves calculated from the SAXS data shown in part (a). (c) and (e) Particle size distribution histograms estimated for the same samples from TEM images.

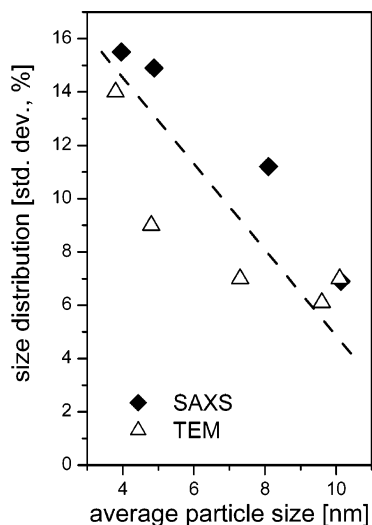


Figure 9. Standard deviation of the particle size distributions observed for as-prepared CoPt₃ nanocrystals of different average size.

have an electron density similar to that of the solvent (hexane). Therefore the SAXS- and HRTEM sizes account only for the inorganic core in the nanocrystal.³⁵

In the case of ~10 nm CoPt₃ nanocrystals the SAXS size distribution curve was superimposed of a peak corresponding to the single particle population and a tail in the large size region (Figure 8d). The TEM investigations of the same sample revealed a symmetric size distribution curve without any features around 12–13 nm (Figure 8e). This allows us to assume partial aggregation of ~10 nm CoPt₃ in hexane at room temperature.¹² Long-term stability of the colloidal solutions as well as the absence of agglomerates in TEM images provides evidence that the aggregation is reversible. Relatively small attractive interactions between ~10 nm CoPt₃ nanocrystals are also evident from the Guinier plots with a concave curvature of the scattered X-ray intensity near the origin.³⁴ Dilution of the colloidal solutions increases the particle aggregation whereas addition of small amount of HDA allows recovering single-particle population. Another factor resulting in some discrepancy between TEM and SAXS data might be shape anisotropy observed in TEM and HRTEM images for large CoPt₃ nanocrystals (Figure 4) which distorts the spherical particle approximation used in our calculations.

The absolute width of the particle size distribution is nearly constant for both, the ~4 nm and the ~10 nm samples (Figure 8). This means that the relative size distribution of as-prepared ~4 nm CoPt₃ nanocrystals is much broader as compared to that of ~10 nm nanocrystals (~14% and ~7% of standard deviation, correspondingly). The width of the size distribution for as-prepared CoPt₃ nanocrystals was plotted against the mean particle size for samples with different average size (Figure 9). The general tendency is a narrowing of the size distribution with increase of the particle size as observed for all samples irrespective of the method of size control. The same trend is seen in the TEM and HRTEM images (Figure 4). Post-preparative size-selective precipitation allows further narrowing of the nanocrystal size distribution.²¹

Faceting of CoPt₃ Nanocrystals. CoPt₃ nanocrystals with sizes smaller than ~7 nm are usually spherical (Figures 4 and S3 from the Supporting Information). However, further increase

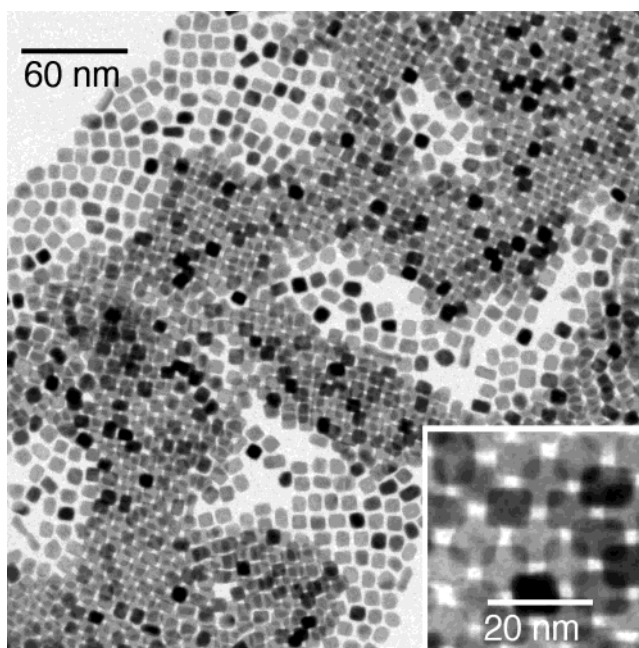


Figure 10. TEM overview image of faceted CoPt₃ nanocrystals prepared at 145 °C. Molar ratio of Pt:Co:ACA was 1:3:6.

of the nanocrystal size results in a rather abrupt transition from spherical to cubic, truncated cubic or, in some cases, platelike shapes as shown in Figure 10. It was also observed that annealing at ~275 °C results in smoothing of the edges of cubic nanocrystals formed at 145 °C (cf., Figures 4d and 10). Each side of cubic crystal lattices corresponds to the [100] direction of the *fcc* nanocrystal lattice. Cubic particles can form if the growth rate in the [111] direction is much higher than that in the [100] direction.³⁶ The ratio between growth rates in different directions can be varied by specific adsorption of organic surfactants onto particular crystallographic facets inhibiting the growth of a particular crystallographic direction.³⁷ Recently, this type of shape control has been demonstrated for the colloidal synthesis of CdSe,³⁸ Pt,¹¹ and Co.^{19,37} nanocrystals. However, the phenomena responsible for the abrupt transition from spherical to faceted particle during growth in a colloidal solution are not clear and require further investigation.

Engineering the nanocrystal shape should allow creating new kinds of superstructures formed from nanocrystals as building blocks. In the case of spherical particles the crystalline lattices of individual nanocrystals are randomly oriented within a superstructure. However, faceted and, in particular, cubic nanocrystals can form “lattice matched superstructures” where each nanocrystal has the same orientation as its neighbors (Figure 10b, inset). Such superstructures are of intriguing interest for materials with high magnetic anisotropy constant because of the possibility to align the easy magnetization axes of individual nanocrystals. CoPt₃ nanocrystals are, probably, superior candidates for realizing this new kind of artificial solids.

(34) Mattoussi, H.; Cumming, A. W.; Murray, C. B.; Bawendi, M. G.; Ober, R. *J. Chem. Phys.* **1996**, *105*, 9890.

(35) Mattoussi, H.; Cumming, A. W.; Murray, C. B.; Bawendi, M. G.; Ober, R. *Phys. Rev. B* **1998**, *58*, 7850.

(36) Wang, Z. L. *Adv. Mater.* **1998**, *10*, 13.

(37) Puentes, V. F.; Zanchet, D.; Erdonmez C. K.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2002**, ASAP article.

(38) Peng, X.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59.

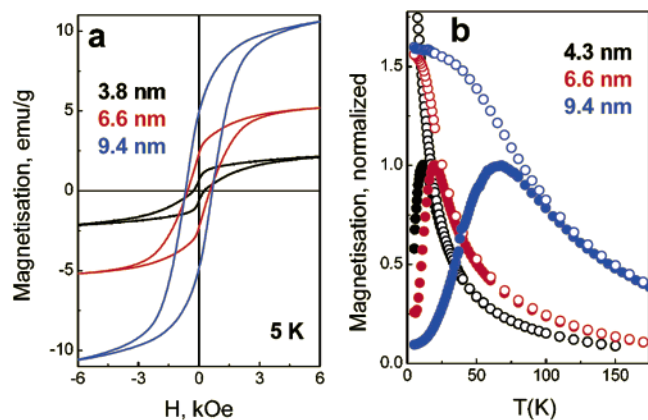


Figure 11. (a) Magnetization vs applied field hysteresis loops measured at 5 K for 3.8, 6.6, and 9.4 nm CoPt₃ nanocrystals. (b) Zero-field-cooled (ZFC) and field-cooled (FC) magnetization vs temperature curves for CoPt₃ nanocrystals of different size (4.3, 6.6, and 9.4 nm).

Size-Dependent Magnetic Properties of CoPt₃ Nanocrystals. Each CoPt₃ nanoparticle is a single-domain magnet. To investigate the magnetic properties inherent to independent nanoparticles, the measurements were performed on ensembles of monodisperse noninteracting nanoparticles. Interparticle interactions were reduced by dissolving the CoPt₃ particles in dodecane at a low concentration (<1 wt. %).¹⁶ Figure 11 shows a set of measurements performed for characterizing the size-dependent magnetic properties of CoPt₃ nanocrystals. The hysteresis measurements performed at 5 K on nanocrystals of different size revealed a decrease of the coercivity with decreasing particle size (Figure 11a). This may be explained by thermal agitation of the particle magnetic moments. The energy barrier between different easy axes of magnetization of a particle scales with the particle volume, implying that the magnetic moment of a small particle more easily reorients because of thermal agitation, thus leading to a decrease of the coercivity.

The drop in the saturation magnetization with decreasing nanoparticle size (Figure 11a) can be attributed to an increase of the surface-to-volume ratio.¹⁶ Hysteresis loop measurements at different temperatures nicely illustrate the transition from blocked particle magnetic moments to a superparamagnetic behavior in CoPt₃ nanocrystals (Supporting Information, Figure S4). With increasing temperature, the thermal agitation of the nanoparticle magnetization directions increases, reducing the coercivity and leading to a superparamagnetic behavior at temperatures above 70 K. More detailed information about the blocking temperatures of the different CoPt₃ nanocrystals can be obtained from the ZFC and FC vs temperature curves shown in Figure 11b. The blocking temperature as estimated from the peak magnetization of the ZFC curves increases with particle size, from 10 K for 4.3 nm up to 70 K for 9.4 nm nanoparticles. A more detailed study of size-dependent magnetic properties of CoPt₃ nanocrystals is given in ref 39.

Discussion

The synthesis of colloidal crystalline particles from a homogeneous solution involves two consecutive stages: formation of nuclei with sizes larger than the critical one (nucleation

stage) and growth of these nuclei (growth stage).⁴⁰ The latter can occur via the following mechanisms: (i) growth consuming molecular precursors from surrounding solution; (ii) Ostwald ripening or coarsening when larger particles grow at the expense of dissolving smaller ones;⁴¹ and (iii) fusion of several particles (oriented attachment).⁴²

Colloidal metal nanocrystals usually grow via the first mechanism, i.e., consuming dissolved molecular species (monomers), whereas neither Ostwald ripening nor oriented attachment is observed.^{10–12,15–18,20,21,24} Ostwald ripening can occur only if the addition of a monomer to a nanocrystal is a reversible process, i.e., a nanocrystal can both consume or release molecular species. In this case, smaller particles which have higher chemical potential evolve monomer and dissolve whereas larger particles consume monomer and grow. This behavior was observed for many semiconductor colloids and is usually used for tuning the mean particle size.^{4,6} In contrast, the transformation of molecular precursors to metal particles is either irreversible or the equilibrium between monomer and solid is strongly shifted toward the solid.

In the absence of Ostwald ripening, it is rather difficult to tune the particle size in a predictable and reproducible manner. Let us consider possible ways of size control on the example of CoPt₃ nanocrystals:

It is principally possible to inject the cobalt stock solution at a low temperature and quench the reaction at an early stage when the nanocrystals are small. However, this approach has serious drawbacks: (i) the particles exhibit poor crystallinity at early stage of the reaction (Figures 2 and 3); (ii) only a small part of the precursors is converted to the nanocrystals; and (iii) in the absence of any means suitable for express monitoring of the particle size (like the color changing in solutions of growing semiconductor nanocrystals) it is difficult to quench the reaction exactly at the desired stage.

Another approach to size tuning could be additional injections of precursors into the reaction mixture.^{20,21} However, in this case nucleation of new particles usually competes with growth of already existing ones.²¹ Moreover, large CoPt₃ and FePt nanocrystals prepared by additional injections are irregularly shaped and possess various lattice defects.^{21,43} Therefore, more easy and facile ways of size-tuning are strongly desirable for CoPt₃ and other metal nanocrystals.

In the case of CoPt₃ nanocrystals, it was found that an increase in the concentration of the stabilizing agent resulted in the increase of the nanocrystal size (Figure 6b). This is rather surprising because conventional routes for Au and Ag nanocrystals usually exhibit opposite behavior.²⁴ Also a higher concentration of stabilizing agent is commonly used also to prepare smaller semiconductor particles. The size dependence of CoPt₃ nanocrystals on the concentration of ACA as well as the number of other experimental data observed for the synthesis of CoPt₃ (Figures 6 and 7) and some other metal nanocrystals can be understood when we consider some peculiarities of the nanocrystal nucleation process. In the absence of Ostwald ripening, particles can grow only until all molecular precursors

(40) Sugimoto, T. *Monodisperse Particles*; Elsevier: 2001.

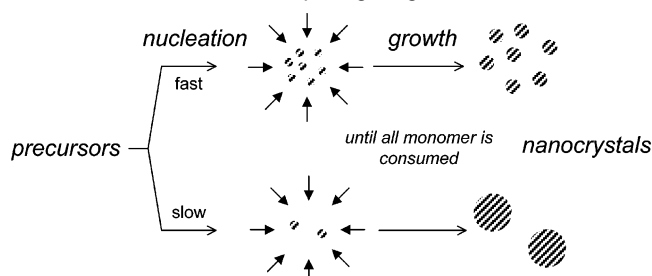
(41) Talapin, D. V.; Rogach, A. L.; Haase, M.; Weller, H. *J. Phys. Chem. B* 2001, 105, 12 278.

(42) Pacholski, C.; Kornowski, A.; Weller, H. *Angew. Chem., Int. Ed. Engl.* 2002, 41, 1188.

(43) Dai, Z. R.; Sun, S.; Wang, Z. L. *Surf. Sci.* 2002, 505, 325.

(39) Wiekhorst, F.; Shevchenko, E.; Weller, H.; Kötzler, J. *Phys. Rev. B* 2003, 67, 224416.

Scheme 1. Schematic Representation of Nanocrystal Synthesis in the Absence of the Ostwald Ripening Stage



are consumed. The total amount of consumed monomers (as well as the total volume of formed particles) is constant. In this case, the balance between the rates of nucleation and growth should affect the final particle size as illustrated in Scheme 1. Fast nucleation provides high particle concentration and yields small particles. Slow nucleation provides low concentration of seeds consuming the same amount of monomer and results in large particles. Thus, a control over the nucleation rate allows tuning of the final nanocrystal size in the absence of Ostwald ripening. The screening of experimental conditions demonstrates the possibility to vary the size of CoPt₃ nanocrystals in a wide range (Figures 6 and 7).

To date, almost no reliable information about the microscopic mechanism and kinetics of nucleation of real colloidal nanoparticles is available.⁴⁴ However, there are some general features inherent to the homogeneous nucleation phenomenon. The classical nucleation theory gives the following expression for the crystal nucleation rate per unit volume (J_N)^{40,44}

$$J_N = B_N \exp\left(-\frac{\Delta G^N}{RT}\right) \quad (1)$$

$$\Delta G^N = \frac{16\pi\gamma^3 V_m^2}{3|\Delta\mu|^2} \quad (2)$$

where ΔG^N is the activation energy for homogeneous nucleation; γ is the surface tension; V_m is the molar volume of solid; $\Delta\mu$ (<0) is the difference in chemical potential between solid and monomers; B_N is the preexponential factor depending on many parameters such as desolvation of species, and so forth.

Effect of the Reaction Temperature. Figure 6a shows the decrease of the CoPt₃ nanocrystal size with increasing reaction temperature. It demonstrates that the nucleation rate raises faster with temperature than the growth rate. Usually, the activation energy for the nucleation process ΔG^N is much higher than that for particle growth.⁴⁰ It means that the nucleation rate is much more sensitive to changes in temperature compared to the growth rate. In fact, this situation is widely used in the organometallic synthesis of semiconductor nanocrystals: the “hot-injection” technique allows temporal separation of nucleation and growth stages because the homogeneous nucleation can be completely quenched via a small temperature drop whereas the growth rate does not undergo such drastic changes.^{4,29} In other words, variation of the reaction temperature affects the nucleation stronger than the growth and, therefore, can be used to adjust the balance between nucleation and growth rates. At higher reaction temperature more nuclei are formed and, according to

the Scheme 1, the final particle size is smaller. In combination with subsequent annealing of the nanocrystal lattice, variation of the reaction temperature provides a powerful tool for size control which can be used to prepare different high quality metal nanocrystals.

Effect of the Concentration of the Stabilizing Agent. The nucleation rate (J_N) can also be adjusted via the parameter $\Delta\mu$ which affects both ΔG^N and B_N in eqs 1 and 2.⁴⁰ The parameter $\Delta\mu$ describing the difference in chemical potential between solid and monomers rises with increase of monomer oversaturation (the simplest relation is $\Delta\mu = RT \ln S$, where the oversaturation S is the ratio between the current and the equilibrium concentration of monomer⁴⁰). Molecules such as ACA, TOPO, TOP, amines, etc. used to passivate the surface of growing nanocrystals can also form stable complexes with individual metal atoms of a molecular precursor (monomer). The formation of such complex precedes the particle nucleation process. For instance, the platinum precursor (Pt(acac)₂) decomposes in the HDA–diphenyl ether–1,2-hexadecandiol mixture at ~ 130 °C. Addition of ACA in the amount commonly used for the synthesis of CoPt₃ nanocrystals increases the decomposition temperature up to ~ 220 °C. A similar behavior was also observed for the cobalt precursor: addition of ACA drastically enhances the stability of the cobalt carbonyl solution against thermodecomposition. Formation of a stabilizing agent – monomer complex increases the equilibrium concentration of the monomer, i.e., it decreases the monomer oversaturation as well as the parameter $\Delta\mu$ in eq 2. Therefore, an increase of the concentration of a stabilizing agent is expected to suppress nucleation and, as a consequence, yields larger nanocrystals (Scheme 1). These predictions are in agreement with the behavior of CoPt₃ nanocrystals: higher initial concentrations of ACA results in a considerable increase of the average nanocrystal size (Figure 6b). In fact, dependencies similar to that shown in Figure 6b for CoPt₃ nanocrystals were recently reported for γ -Fe₂O₃,¹⁵ prepared via oxidation of preformed iron seeds and for Pt nanocrystals prepared via a relatively “hot” synthesis.¹⁰

Dependence of the Nucleation Rate on the Ratio between Co and Pt Precursors. We varied the initial concentrations of Co and Pt precursors keeping all other parameters constant. As it has been discussed above, the final nanocrystal size depends mainly on the balance between the particle nucleation and growth rates. Probably, one may apply this approach to the inverse task, i.e., use the final size of the CoPt₃ nanocrystals as a probe of the balance between nucleation and growth rates.

An increase of the concentration of cobalt precursor results in a decrease of the particle size (Figure 7a). In accord with our model (Scheme 1), this can be explained by an increase of the nucleation rate for CoPt₃ nanocrystals. For high concentration of cobalt precursor, more nucleation seeds are generated and as a result the CoPt₃ nanocrystals of smaller sizes are formed. Actually, the observed behavior could also be explained by a decrease in particle growth rate due to increasing the concentration of cobalt precursor. However, the nanocrystal growth process with the negative reaction order with respect to the cobalt precursor seems to be very doubtful.

An increase of the concentration of the Pt precursor results in an increase of the size of CoPt₃ nanocrystals (Figure 7b). We always used some excess of the Co-precursor with respect

(44) Auer, S.; Frenkel, D. *Nature*, **2001**, *409*, 1020, and references therein.

to the 1:3 ratio given by the CoPt₃ formula. Therefore, the nanocrystals should grow until all Pt is consumed. The increase of the particle size results from the termination of the particle growth at a later stage. Surprisingly, the linear dependence of cube of particle size (approximate particle volume) on the concentration of Pt precursor was observed in the wide range of Pt-to-Co ratios (Figure 7b). This provides evidence that the number of formed nuclei is constant and does not depend on the initial concentration of Pt or, in other words, the nucleation rate of CoPt₃ nanocrystals has 0-th kinetic order with respect to Pt(acac)₂. A deviation from this behavior was observed only in the case of high platinum concentrations (Figure 7b) and can be explained by some increase of the number of formed nuclei at very high concentration of the Pt-precursor. As mentioned above, ACA can form complexes both with cobalt and platinum precursors. When the concentration of the Pt-precursor is very high, a considerable amount of ACA is consumed by platinum, and, therefore, less amount of ACA is available for the stabilization of the Co-precursor. As a result, the nucleation rate can slightly vary with the concentration of the Pt-precursor even if it does not directly participate in the nucleation process (see below).

We have also studied the preparation of pure Co and pure Pt nanoparticles in ACA-HDA mixture under identical reaction conditions. As a result, we obtained a transparent blue solution in the case of prolonged heating cobalt carbonyl without any traces of crystalline material, whereas the respective experiment with Pt(acac)₂ resulted in the formation of bulk *fcc* platinum which precipitated immediately.²¹ Moreover, the influence of the nature of the cobalt and platinum precursors on the final size of CoPt₃ nanocrystals was studied. If cobalt acetylacetonate (Co(acac)₂) is injected into the reaction mixture at 170 °C instead of Co₂(CO)₈, then the size of CoPt₃ nanocrystals (~11.5 nm) was considerably larger than the size of the nanocrystals prepared according to the conventional method (~6.2 nm). Probably, in the case of more stable Co(acac)₂ the nucleation rate was considerably slower. On the other hand, when we performed the synthesis of CoPt₃ nanocrystals at 170 °C in the absence of 1,2-hexadecandiol which affects mainly the reduction rate of Pt(acac)₂,²⁰ the mean nanocrystal size (~6.3 nm, the TEM image is shown in the Supporting Information, Figure S5) was nearly equal to that of nanocrystals prepared via the conventional method (6.2 nm). This seems to be another strong hint that the platinum precursor does not determine the nanocrystal nucleation rate.

Discussion of the Nucleation Mechanism. It is extremely complex to investigate the microscopic nucleation mechanism. The difficulty originates from basics of the nucleation phenomenon: the bottleneck for the nucleation process is the formation of critical nuclei which are *the most unstable species* with the highest chemical potential in the reaction mixture.⁴⁴ As a result, the critical nuclei are present at a concentration so tiny that their structural characteristics cannot be probed by existing methods. Moreover, the phase that nucleates needs not be the one that is thermodynamically stable.⁴⁵ This opens up a broad field of speculation about the peculiarities of the nucleation process in a given system. Probably, independence of the nucleation rate of the concentration of the platinum precursor means that the

critical nuclei for CoPt₃ nanocrystals consist only of Co. In other words, the growth of the nanocrystals starts from the formation of Co clusters, which serve as seeds for further growth of CoPt₃ particles. In fact, such polynuclear cobalt carbonyl clusters, e.g., Co₄(CO)₁₂ and Co₆(CO)₁₆, form as intermediates upon the thermal decomposition of Co₂(CO)₈.³⁷ When the concentration of the cobalt precursor increases, the number of these Co-seeds also increases (smaller CoPt₃ nanocrystals form) whereas a concentration change of the platinum precursor does not affect the number of the Co-seeds.

The initial cobalt seeds are, probably, some clusters consisting of only a few atoms. These seeds after covering with a platinum-rich shell can easily be converted into a uniform alloy by mutual diffusion. Such atomic diffusion can definitely take place during the nanocrystal annealing at ~280 °C. Also, cobalt seeds can interact with Pt(acac)₂ via the transmetalation reactions⁴⁶ directly forming a cobalt–platinum alloy.

Recently, Ciacchi et al. reported a theoretical investigation of possible pathways for the nucleation of Pt nanocrystals after reduction of Pt(II) salts both in gas phase and in solution.⁴⁷ Their calculations as well as the experimental observations by Henglein et al.⁴⁸ have ruled out Pt(0) atoms as reaction intermediates. In contrast, reduction of Pt(II) to Pt(I) is followed by the formation of Pt(I)–Pt(II) dimers. Interestingly, the addition of ions to a growing cluster takes place before their reduction to the metallic state.⁴⁷ Probably, Pt(II) can also be attached to a polynuclear cobalt carbonyl cluster (nucleation seed) with further reduction of the entire cluster and followed by an iterated reduction/addition mechanism of growth of Co–Pt clusters. Reducing agent in this case can be either α -diol (1,2-hexadecandiol) or CO-ligands. As was reported by Gogging et al.,⁴⁹ CO can reduce Pt(II) in solution and, simultaneously, be a ligand stabilizing the Pt(I) intermediate. When we tried to perform the synthesis in the absence of 1,2-hexadecandiol using Pt(acac)₂ and Co(acac)₂ as precursors, no nanocrystals were formed at 170 °C. We also found that the presence of 1,2-hexadecandiol is important if the synthesis is performed at 145 °C from Co₂(CO)₈ and Pt(acac)₂ because slow reduction of Pt(acac)₂ by CO ligands at a low-temperature results in broader size distribution. A very interesting and still unanswered question is why the nanocrystals always retain their CoPt₃ stoichiometry despite the existence of other stable cobalt–platinum intermetallic compounds? One assumption might be that the constant Co-to-Pt ratio is a result of the complex reduction mechanism of Pt(II) involving interactions with a certain number Co atoms supplying their CO ligands.

Size Distribution of the CoPt₃ Nanocrystals in Growth. Progressive narrowing of the particle size distribution with increasing mean size was observed for CoPt₃ nanocrystals (Figures 8, 9). The size distribution of colloidal nanoparticles was a subject of many investigations.^{40,41,50} Thus, if nanoparticles grow via Ostwald ripening, the particle size distribution tends to the unique one irrespective of the initial shape of the size distribution.^{41,51} On the other hand, if nanocrystals grow

(45) Klein, W.; Leywraz, F. *Phys. Rev. Lett.* **1986**, *57*, 2848.

(46) Park, J.-I.; Cheon, J. *J. Am. Chem. Soc.* **2001**, *123*, 5743.

(47) Ciacchi, L. C.; Pompe, W.; De Vita, A. *J. Am. Chem. Soc.* **2001**, *123*, 7371.

(48) Henglein, A.; Giersig, M. *J. Phys. Chem. B* **2000**, *104*, 6767.

(49) Gogging, P. L.; Googfellow, R. *J. Chem. Soc., Dalton Trans.* **1973**, 2355.

(50) Peng, X.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343.

(51) Wagner, C. Z. *Elektrochem.* **1961**, *65*, 581.

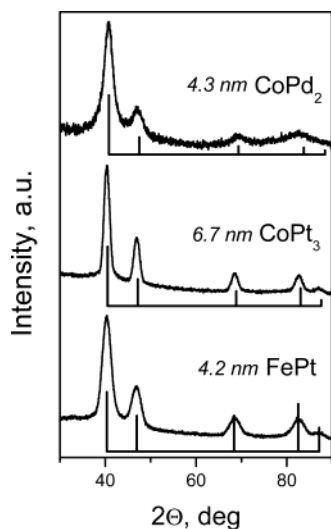


Figure 12. Typical powder-XRD patterns of FePt, CoPt₃ and CoPd₂ nanocrystals synthesized in the ACA-primary amine stabilizing mixture. The average nanocrystal sizes were calculated by the Debye-Scherrer equation and from TEM investigations.

consuming molecular precursors from surrounding solution, the size of smaller particles increases faster than that of the larger ones.⁴⁰ In this case, an increase of the mean particle size is accompanied by a narrowing of the initial particle size distribution, which keeps nearly symmetric during particle growth.⁴¹ This growth regime was recently observed for ensembles of CdSe nanocrystals and was called “focusing” of size distribution.⁵⁰ As was discussed above, CoPt₃ nanocrystals can grow only by consuming the monomers from solution, i.e., in the “focusing” mode. This explains the observed narrowing of the size distribution with increase of the particle size (Figure 9).

Hot Organometallic Synthesis of Other Metal Nanocrystals. As was mentioned above, our concepts developed for the preparation of CoPt₃ nanocrystals are also applicable for the “hot” synthesis of some other metal nanocrystals such as Fe¹⁵ and Pt.¹⁰ We also investigated another very interesting system, FePt, to reveal an easy method of size control of FePt nanocrystals. The original recipe by Sun et al. yields ~3 nm FePt nanocrystals and the particle size was tuned only via additional injections of precursors.²⁰ In the presence of oleic acid and oleylamine, the original capping ligands for FePt nanocrystals, Pt(acac)₂ starts to decompose at ~130 °C what makes difficult tuning of the particle size via variation of the reaction temperature (e.g., Figure 6a). That is why we adopted our ACA–primary amine approach for the preparation of PtFe nanocrystals. Thus, the synthesis of FePt nanocrystals was performed in the ACA–dodecylamine coordinating mixture. Injection of the Fe(CO)₅ stock solution at 170 °C results in the formation of nearly monodisperse ~4.8 nm nanocrystals with the composition close to Pt₄₈Fe₅₂ (Figure 12, see details in the Supporting Information). An increase of the injection temperature up to 215 °C resulted in a decrease of the average nanocrystal size to ~3.5 nm and a broader size distribution. Unfortunately, the reaction is too slow at temperatures below 170 °C, which did not allow us to prepare larger FePt nanocrystals in the ACA–dodecylamine mixture in a reasonable time window. The range of available sizes of FePt nanocrystals can be extended when HDA or octadecylamine are used instead of dodecylamine (see the Supporting Information). A considerable decrease of the average nanocrystal

size was always observed with increasing reaction temperature, however, as-prepared FePt nanocrystals larger than ~6 nm usually have rather irregular shapes. Moreover, a variation of the nanocrystal composition was observed when the initial ratio of the iron and platinum precursors was changed.²⁰ This makes the FePt nanocrystal synthesis more complex for studying as compared to the CoPt₃ synthesis.

CoPd₂ nanocrystals can also be prepared by the ACA approach in pure HDA or HDA–diphenyl ether coordinating mixture (Figure 12). However, the preparation of CoPd₂ nanocrystals has some different features in comparison with the synthesis of CoPt₃ nanocrystals. In the ACA–HDA mixture, Pd(acac)₂ starts to decompose at relatively low temperature (~125 °C) yielding irregularly shaped polydisperse Pd nanocrystals. This makes tuning the particle size via variation of the reaction temperature rather difficult. Also, if the concentration of ACA is high enough, the Co-precursor formed a too stable complex with ACA and the synthesis resulted in formation of Pd nanocrystals. However, the proper choice of the molar ratio between Co precursor and ACA is a key point of the synthesis of high quality CoPd₂ nanocrystals. Variation of the injection temperature as well as the ratio between the palladium and cobalt precursors allowed tuning the size of CoPd₂ nanocrystals with the same tendencies as in the case of CoPt₃ nanocrystals. For instance, injection of cobalt precursor at 125 °C resulted in the formation of ~3.5 nm crystals while the injection at 100 °C allowed increasing the size of CoPd₂ nanocrystals up to ~6 nm.

Detailed studies aimed to achieve the size and the composition control for FePt and CoPd₂ nanocrystals are currently underway.

Conclusions

High quality CoPt₃ nanocrystals with narrow size distribution and mean particle size between ~3 nm up to 18 nm can be prepared in a predictable and reproducible manner via simultaneous reduction of platinum acetylacetonate and thermodecomposition of cobalt carbonyl in the presence of 1-adamantanecarboxylic acid and hexadecylamine as stabilizing agents. From the investigation of the effect of different reaction conditions (reaction temperature, concentration of the precursors and stabilizer) on the nanocrystal synthesis, we conclude that the size control achieved in this system is of purely kinetic nature. Nanocrystal size control in systems without the Ostwald ripening stage can be achieved via control over the balance between the nucleation and growth rates. We demonstrated on an example of CoPt₃ nanocrystals that slower nucleation results in the formation of larger nanocrystals with narrower size distribution (st.div. ≈ 7%), while fast nucleation yields smaller nanocrystals with broader (st.div. ≈ 14%) size distributions. The CoPt₃ nanocrystal size increases with increasing of the concentration of stabilizer (1-adamantanecarboxylic acid). This effect was attributed to the slower rate of nucleation at high concentration of the stabilizer. Such behavior seems to be typical of the hot organometallic syntheses of metal nanocrystals and was observed also in the preparation of Fe, Pt as well as FePt and CoPd₂ nanocrystals. The possibility of the formation of faceted cubic CoPt₃ nanocrystals was also shown.

The experimental results seem to indicate that nucleation of CoPt₃ nanocrystals occurs on some cobalt seeds forming via thermodecomposition of cobalt carbonyl. The formation of these clusters is the rate-limiting step for the whole nucleation process,

whereas the concentration of platinum precursor does not affect the nucleation rate. A possible microscopic nucleation mechanism is discussed.

The development of new methods of precise size control of CoPt₃ nanocrystals allows the investigation of their size-dependent magnetic properties.

Acknowledgment. We thank Prof. Dr. S. Förster and Dr. K-H. Klaska for helpful discussions, Prof. J. Kötzler and F. Wiekhorst for magnetic measurements on our samples. Special appreciations go to S. Bartholdi-Nawrath for assistance with the TEM measurements and to R.-M. Pakula for carefully reading the manuscript. This work was supported by the EU research project BIOAND and the Deutsche Forschungsgemeinschaft through the SFB 508.

Supporting Information Available: Detailed description of preparations of CoPt₃ nanocrystals with different sizes (Table S1); Temporal evolution of the absorption spectra of crude solutions during synthesis of CoPt₃ nanocrystals at 145, 170, and 200 °C (Figure S1); Evolution of the XRD nanocrystal size upon annealing at 275 °C (Figure S2); HRTEM image showing perfect crystallinity of annealed CoPt₃ nanocrystals (Figure S3); Magnetic hysteresis loops for 9.4 nm CoPt₃ nanocrystals measured at different temperatures (Figure S4); TEM and HRTEM images of CoPt₃ nanocrystals prepared without 1,2-hexadecandiol (Figure S5); Size control of FePt nanocrystals as well as their TEM and HRTEM images (Table S2, Figure S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA029937L