

Synthesis of Core–Shell PtCo Nanocrystals<sup>†</sup>Nelli S. Sobal,<sup>\*,‡,§</sup> Ursula Ebels,<sup>||</sup> Helmuth Möhwald,<sup>§</sup> and Michael Giersig<sup>\*,‡</sup>

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Monodisperse, bimetallic PtCo nanoparticles with a controllable core–shell structure have been synthesized by a new two-stage route. The process involves thermal decomposition of cobalt carbonyl in the presence of a nanosized platinum (Pt) dispersion, where the thickness of the Co shell can be controlled by changing the amount of cobalt carbonyl. The synthesized particles reveal a narrow size distribution with average diameters of 2.6 for Pt and a maximum of 7.6 nm for PtCo. Transmission electron microscopy (TEM), energy-dispersive X-ray spectrometry (EDX), optical spectroscopy, and superconducting quantum interference (SQUID) magnetometry were used for characterization of the bimetallic system.

## Introduction

Many of the physical phenomena that make metallic nanoparticles so widely applicable are highly size-dependent. Therefore, the precise synthesis and characterization of nanoscale metallic materials is of great interest for such exploits as magnetic recording,<sup>1,2</sup> catalysis,<sup>3–8</sup> nanoelectronics,<sup>9–12</sup> nanoscale optics,<sup>13</sup> and materials science.<sup>14–16</sup> In particular, a significant number of recently published papers are concerned with magnetic colloidal particles, whose attractiveness stems from their possible application to magnetic data storage media. Methods for preparing highly disperse individual magnetic crystals of Co,<sup>17–25</sup> Fe,<sup>20,26,27</sup> and Ni<sup>20</sup> have been described. One can apply the technique of Sun and co-workers,<sup>28</sup> originally proposed to generate FePt, to prepare alloyed nanoparticles such as CoPt<sub>3</sub>,<sup>29</sup> FePt,<sup>28,30–32</sup> FeCoPt,<sup>33</sup> CoPt,<sup>34</sup> FeMo,<sup>35</sup> and FePd.<sup>34</sup> The properties of such small particles depend on their composition, shape, and method of preparation. Therefore the formation of alloys thoroughly explains new properties of magnetic systems, often distinct from those of the corresponding monometallic particles. FePt, PtCo, and Pt<sub>3</sub>Co alloys show high magnetic anisotropy and chemical stability in comparison to pure Fe and Co metallic colloids.<sup>36,37</sup> Nunomura et al.<sup>38</sup> have observed a large increase of the magnetic moment in PdNi particles above a threshold concentration of 6.3 atom % Ni. Self-assembled films of Fe<sub>x</sub>Co<sub>y</sub>Pt<sub>100–x–y</sub> alloy particles have lower coercivity than FePt samples.<sup>33</sup> The authors of ref 39 noticed a promotion of the fcc to tetragonal phase transition and an increase in coercivity of the films as a result of adding Ag to FePt nanocrystals.

Besides monometallic or alloy structured particles, core–shell-type systems are of great interest and have revealed a large range of ferromagnetic properties. Results have been reported for metallic<sup>40–47</sup> and alloyed<sup>48,49</sup> core particles covered with a noble metal (usually Au or Ag). However, in the absence of

any systematic investigation of such crystals, it has not been possible to find any regularity in their properties or to verify chemical structure.

In this paper we focus on a “reverse” core–shell particle system, where a noble metal core of Pt is surrounded by a magnetic Co shell. In a previous article<sup>50</sup> we have already shown that Ag-core/Co-shell nanocrystals exhibit optical activity and magnetic behavior distinct from that peculiar to both noble and 3d metals. In addition, the presence of a noble metal seems to improve the stability of nanosized Co against oxidation. Any CoO was found even in 3-month-old Co@Ag samples by electron energy loss spectroscopy (EELS) analysis.<sup>51</sup> Bimetallic systems of this sort are expected to reveal interesting magnetic properties as found in analogously constructed continuous films, for instance, an induced polarization in Pt at the Co/Pt interface<sup>52</sup> or a giant magnetoresistance effect as in the case of Pd particles covered with Ni.<sup>53</sup>

## Experimental Section

The so-called modified “polyol” process has been used for preparation of bi- and trimetallic magnetic nanocrystals.<sup>29–31,33,34</sup> In all cases, the reduction of platinum acetylacetonate with a long-chain polyol in the presence of stabilizers was combined with the simultaneous thermal decomposition of cobalt or iron carbonyl. As a result, alloyed particles with a narrow distribution were obtained. Farrell et al.<sup>54</sup> used tiny particles of platinum as nuclei for further synthesis of monodisperse iron particles. Afterwards, the metallic platinum particles are not extracted from the solution and investigated.

In this paper we present a two-stage procedure for the preparation of bimetallic Pt@Co particles. Pure platinum particles with definite diameter were formed at first. Later, decomposition of cobalt carbonyl on the Pt seeds, if carried out at relatively low temperature, aborts formation of any alloy yielding only Pt-core/Co-shell particles. A typical synthesis is described in detail below.

In a three-necked round-bottom flask, a solution of platinum acetylacetonate (99.99%, Aldrich, 0.05 g or 0.125 mmol), 1,2-hexadecanediol (90%, Aldrich, 0.1 g or 0.38 mmol), oleic acid (99+%, Aldrich, 40  $\mu$ L or 0.125 mmol), and oleylamine (70%, Aldrich, 56  $\mu$ L or 0.175 mmol) in 5 mL of diphenyl ether (dpe)

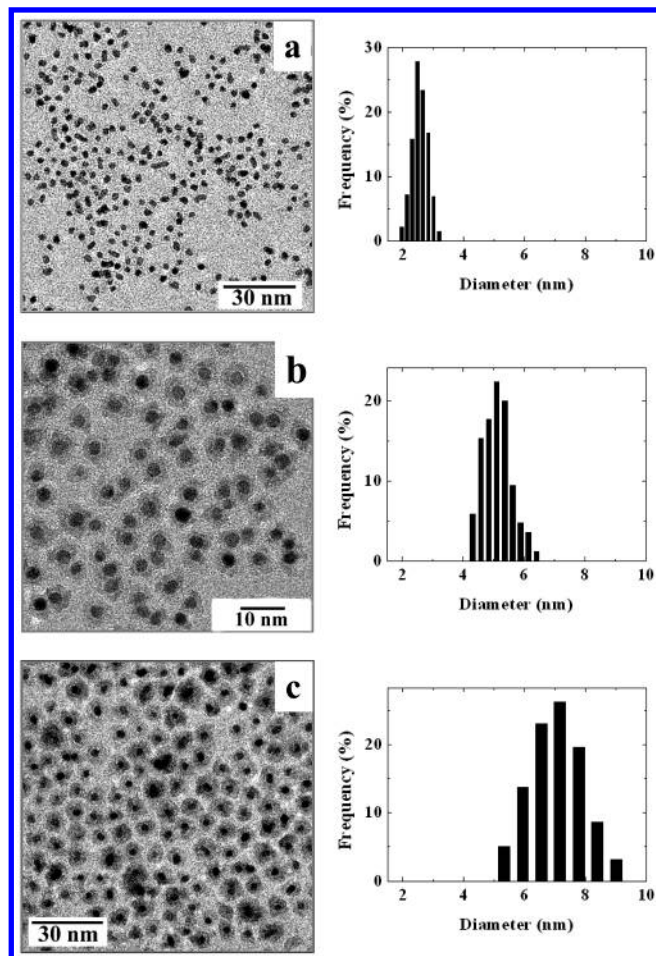
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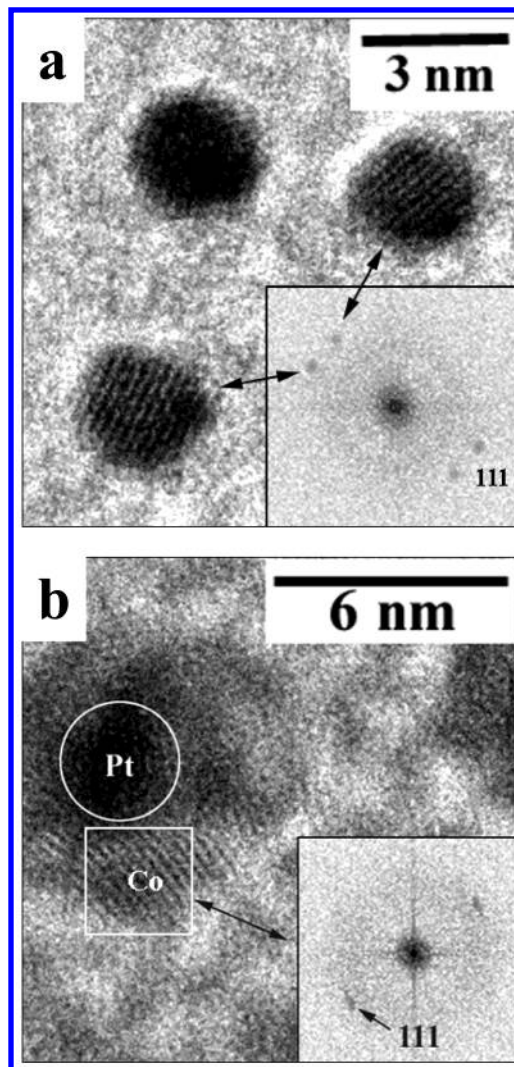
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**Figure 1.** TEM images and size distribution of individual platinum nanoparticles (a) and of Pt@Co nanoparticles prepared at molar ratios Pt:Co<sub>2</sub>(CO)<sub>8</sub> = 1:2 (b) and 1:4 (c).

was heated to 205 °C. After heating for 60 min, the dark mixture was cooled to 142 °C, and the solution of the designed amount of dicobalt octacarbonyl Co<sub>2</sub>(CO)<sub>8</sub> (contains 1–5% hexane as stabilizer, Alfa Aesar) in dpe was gradually added under a nitrogen atmosphere. Mixing and heating at this temperature was then continued for 30 min. The resulting dispersion was left to cool to room temperature, and ethanol was added to precipitate the particles. After removal and drying of the supernatant, the magnetic particles were redispersed in toluene. Use of other nonpolar solvents such as hexane, octane, or chloroform is possible as well.

The structure of the particles was assessed by a transmission electron microscope Philips 12CM, operating at 120 kV, which was equipped with an X-ray fluorescent analyzer for the determination of the material compositions. Samples were prepared by drying a drop of the solution on a thin (5 nm) carbon-film-covered copper grid. The size distribution of the particles was measured from TEM images with at least 200 particles. The UV–visible spectra were recorded on a Bruins spectrophotometer with correction for toluene background absorption. The magnetic measurements were made on a commercial superconducting quantum interference magnetometer (SQUID) from Quantum Design for the M–H loops and from SHE for susceptibility measurements. M–H loops were taken for samples prepared by drying several drops of solution on a Si/SiO<sub>2</sub> substrate, while the zero-field-cooled (ZFC) and field-cooled (FC) data were taken for the liquid solution.



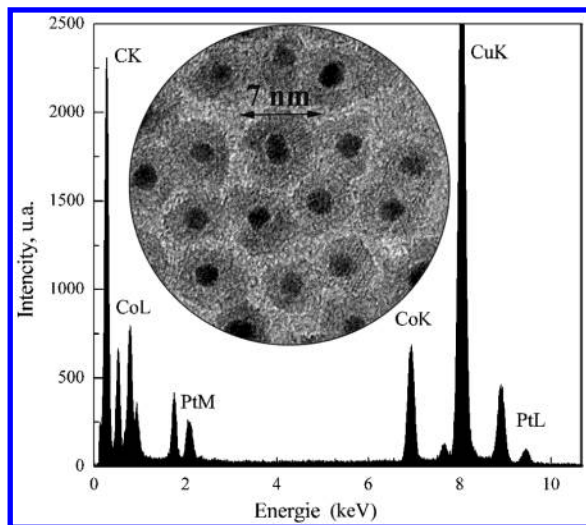
**Figure 2.** HRTEM images of (a) Pt particles with inserted power spectrum showing the typical 111 reflexes for cubic structure and (b) a Pt@Co particle showing the typical lattice plane from a cubic cobalt shell on the Pt particle surface.

## Results and Discussion

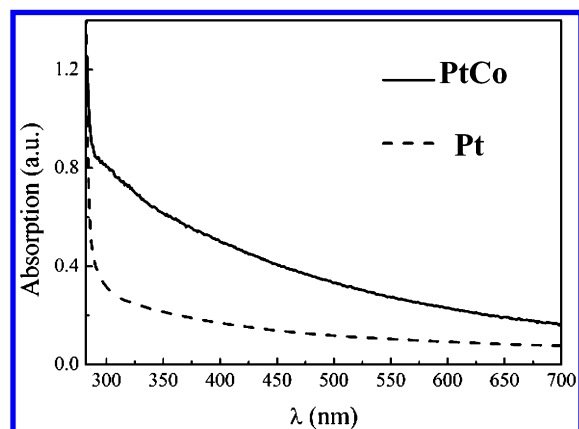
Reduction of platinum acetylacetonate in the presence of surfactants (oleic acid and oleylamine) begins at 180 °C. It was found that 1 h of heating at 205 °C is enough for complete reduction of the platinum salt and formation of a dark-brown colloid of pure platinum. Figure 1a shows the TEM images of individual Pt nanoparticles and the corresponding size histogram. The spherical particles are well-separated and monodisperse with a main size of 2.6 nm (standard deviation, 10%). Figure 1b,c shows the same particles after decomposition of cobalt carbonyl, leading to deposition of metallic cobalt on the surface of the Pt seeds.

Results from examination of uncovered and covered particles by high-resolution TEM are presented in Figure 2a and clearly show the lattice planes with the periodicity of 0.22 nm typical for a cubic crystallographic platinum structure. In Figure 2b, the Pt@Co particles have a measured lattice spacing of 0.20 nm, corresponding to the fcc structure of cobalt nanocrystals.

Additionally, the presence of both Pt and Co metal was qualitatively confirmed by energy-dispersive X-ray (EDX) spectrometric analysis, as is depicted in Figure 3. It is evident that the Pt cores are covered with a brighter layer of cobalt.



**Figure 3.** Typical EDX spectrum of Pt@Co particles, which are shown in the inset. The carbon and copper maxima belong to the TEM grids.

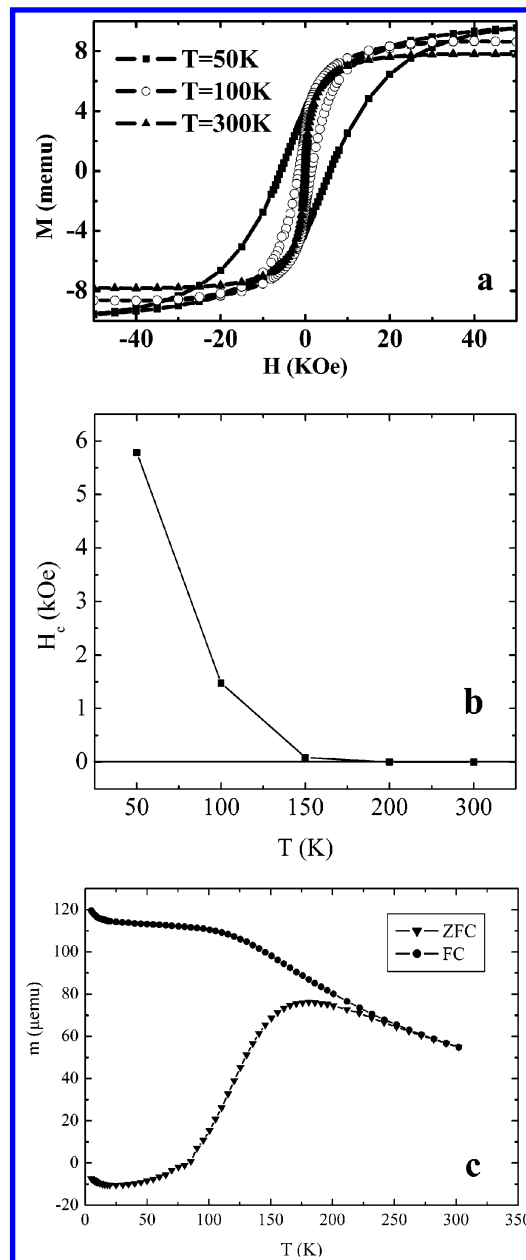


**Figure 4.** Absorption spectra of colloidal solution of Pt in toluene–diphenyl ether (200:1) mixture and of bimetallic Pt@Co particles in toluene.

This result, in agreement with theory, contradicts previously published results for core–shell systems<sup>40–47</sup> wherein the covering of magnetic cores by metals was proposed but not unequivocally presented.

The thickness of the relatively uniform Co shell can be controlled by varying the amount of dicobalt dicarbonyl. Figure 1b,c shows two samples of Pt@Co particles prepared at molar ratios Pt:Co<sub>2</sub>(CO)<sub>8</sub> = 1:2 and 1:4, respectively. The average diameter of the particles in Figure 1b was 5.1 nm and the size distribution remained relatively narrow. The maximum thickness of Co ( $2.3 \pm 0.2$  nm) deposited in this way was reached by the ratio platinum:cobalt dicarbonyl 1:4 (Figure 1c). In this case, the main diameter of the spherical bimetallic particles increased to 7.5 nm, while the size distribution increase to 18%. With more generous amounts of cobalt precursors Pt/Co<sub>2</sub>(CO)<sub>8</sub> = 1:5, the synthesis yields the expected Pt-core/Co-shell particles and some individual Co particles. Incomplete coverage was observed due to cobalt island formation on the platinum surface caused by an accidental decrease in the initial ratio of Pt:Co dicarbonyl below 1:2.

The optical spectra in Figure 4 of Pt and Pt@Co solution show an increased absorption within the shorter wavelength region with no maximum in the region 290–750 nm. In the low wavelengths before 300 nm, the actual information of the particles could not be detected because of the high absorption of toluene.



**Figure 5.** (a) Magnetization vs. field measurements at various temperatures for Pt@Co particles deposited on a Si substrate; (b) variation of the coercive field  $H_c$  as a function of temperature; (c) ZFC/FC magnetization curves measured on 7.5 nm Pt-core/Co-shell nanoparticles dissolved in toluol. The small increase of the magnetic moment in the FC and ZFC data at low  $T$  (below 15 K) might be due to the presence of paramagnetic Pt phase in the solution.<sup>47</sup>

From the magnetic measurements, the particles reveal a superparamagnetic behavior at room temperature, while below 150 K a clear magnetic hysteresis is obtained (see Figure 5a) with a coercivity that falls off with increasing  $T$  (see Figure 5b). The blocking temperature  $T_B$ , below which ferromagnetism sets in, is not defined well due to the distribution of the particle volume and possibly the magnetic properties (such as anisotropy constants). From the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of the 7.5 nm Pt@Co particles (Figure 5c) and the magnetization versus applied field measurements (Figure 5a), the blocking temperature is estimated to lie between 175 and 225 K. This value is much higher than observed for similar-sized  $\beta$ -Co nanocrystals: 55 K for 7.6 nm agglomerated particles<sup>24</sup> and 63 K for self-assembled and 58 K



for isolated 5.8 nm Co,<sup>55</sup> but is similar to values found for 7–8 nm Co core particles surrounded by a CoO shell.<sup>56</sup>

From the blocking temperature, the anisotropy energy density, responsible for blocking the spins into a ferromagnetic state below  $T_b$ , can be estimated by  $25k_B T_B = KV$  as described by Bean and Livingston.<sup>57</sup> Using for the Co shell volume 157 and 127 cm<sup>3</sup>, which corresponds to the 7.5 and 7 nm particles respectively (with a 2.5 nm Pt core) and  $k_B$  the Boltzmann constant, the anisotropy constant  $K$  is on the order of  $4.8 \times 10^6$  erg/cm<sup>3</sup>. This value, is close to both the bulk hcp Co value ( $K = 5 \times 10^6$  erg/cm<sup>3</sup>)<sup>58</sup> and the bulk fcc value ( $K = 2.7 \times 10^6$  erg/cm<sup>3</sup>).<sup>55</sup> Since TEM observation indicates an fcc Co phase, the slightly larger value might be explained by additional energy terms such as surface anisotropy or exchange bias for oxidized Co—surface or dipolar interaction between the particles. These contributions have not been taken into account and need further investigation.

## Conclusion

In summary, we report a new method for the synthesis of small platinum particles in organic solvent with an average diameter of 2.5 nm. By use of this, we also found the synthesis route for the production of Pt@Co colloidal nanoparticles with controllable core–shell structure. This has never been done in such a way before. From magnetic measurements a high blocking temperature has been found.

We shortly plan to arrange bimetallic Pt@Co particles with various amounts of Co in ordered 3D arrays for investigation of collective magnetic properties such as possible GMR effects as found in PtCo thin films or in the PdNi bimetallic nanocrystals described by Teranishi and Miyake.<sup>53</sup>

Palladium- and silver-coated Co nanocrystals could be synthesized by our approach as well. The results as well as X-ray diffraction (XRD) investigation will be published later.

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