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Shape-Selective Synthesis of Palladium Nanoparticles Stabilized by Highly Branched Amphiphilic Polymers**

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Despite the current broad interest in such materials, the synthesis of defined structures in the size range of 10 nm to ca. 1 μm ("mesoscopic") is challenging. Few routes shape selectively afford geometrically regular structures, other than the typical spherical metal particles of 1 to 10 nm. Moreover, these few routes are largely restricted to aqueous systems, however, for catal ysis and other applications dispersions in organic solvents are desirable. Carbon monoxide reduction of a palladium(II) com pound in combination with stabilization by (readily available) amphiphilic hyperbranched polymers surprisingly affords disper sions of hexagonal platelets selectively with average sizes of thirty to several hundred nanometers in toluene. The size can be controlled by the polymer composition. Transmission electron microscopy (TEM), electron diffraction, and extended X ray ab sorption fine structure (EXAFS) spectroscopy demonstrate these palladium(0) platelets to be extremely thin (1 2 nm). Despite this high aspect ratio, the platelets prove quite shear resistant.

1. Introduction

Particulate structures with sizes of 1 μm down to about 1 nm, i.e., the colloidal range, are becoming of increasing inter est. At the lower end of this size scale (1 10 nm) the transition from bulk properties to those of molecules occurs. Such small particles of semiconductors or metals are of interest, e.g., for optoelectronics or catalysis.[1] Slightly larger structures (beyond ca. 10 nm) have been designated the rather general term "me soscopic". Such "mesoscopic" systems are of interest, e.g., for potential applications as functional surfaces.

The synthesis of metal nanoparticles and their properties have attracted considerable attention for more than a cen tury.[2] They may be prepared by various synthetic routes, such as reduction of metal salts in the presence of suitable low mo lecular weight or polymeric stabilizers,[2] electrochemical prep aration,[3] decomposition of organometallic precursors,[4] or va por deposition methods.[5] Most often, spherical particles with sizes in the range of 1 to 10 nm are obtained. However, it has long been known that geometrically regular particles can also be obtained under suitable conditions.[6] Despite recent ad vances towards an understanding of the factors controlling par ticle shape, particularly with respect to the effect of stabilizers on selective crystal growth,[7] successful shape controlled parti cle synthesis is somewhat empirical to date. An early example of the synthesis of geometrically regular palladium nanoparti cles was reported by Turkevich and Kim, who described the formation of a mixture of trigonal, pentagonal, hexagonal, and other palladium particles by formate reduction with sodium polyacrylate as a stabilizer.[6d] Such particles can also be pre pared selectively, assisted by polymers[6e] or low molecular weight stabilizers.[7e–g] Studies on the shape selective synthesis of metal nanoparticles with defined shapes have focused on particles smaller than 20 nm. Only a few examples of the syn thesis of larger, geometrically regular particles with sizes of 20 nm to approximately 100 nm, particularly with high aspect ratios, by convenient methods exist.[8]

The majority of work on nanoparticles with a defined shape has focused on aqueous systems.[9] For catalysis of organic reac tions and other applications, stable solutions of metal nanopar ticles in apolar, inert organic solvents are desirable.

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2. Results and Discussion

Amphiphilic polymers with a hyperbranched, polar scaffold and an apolar periphery efficiently stabilize metal nanoparticles in apolar, inert organic solvents.[10–12] The polar, flexible scaffold interacts with the metal particle surface; the apolar moieties provide solubility in organic solvents, such as toluene. Hyperbranched polymers[13] are randomly branched (degree of branching,[14] DB, ca. 60 %) in comparison to dendrimers,[15] which ideally possess a perfectly branched structure (DB = 100 %). Similar to dendrimers, the highly branched nature of hyperbranched polymers results in a low crystallinity, a low viscosity, and a high solubility in many solvents. Moreover they possess a large number of functional end groups. Albeit that they are not monodisperse, hyperbranched polyethyleneimine and polyglycerol can be prepared with a narrow molecular weight distribution (weight average molecular weight/number average molecular weight, $M_w/M_n < 1.5$) in a single step protocol and are available commercially.[16–17]

For the present study, amphiphilic polymers obtained by partial esterification with fatty acids of a polyglycerol core (DB = 61 %),[18] or by amidation of polyethyleneimine (DB = 60 %), respectively, were employed.[11,19] In both cases amphiphilic molecules result, which have no tendency for extensive aggregation in toluene solution, as evidenced by small angle neutron scattering (SANS, radius of gyration, $R_g < 5$ nm for 1 % toluene solutions).[10b,11,20] Amphiphilic polyglycerols based on different core molecular weights ranging from $M_n = 2000$ g mol^{-1} to $M_n = 10\,000$ g mol^{-1}, partially esterified (22 to 100 %) with two different hydrocarbon substituents OC(=O)R (R = Pentadecyl (C15) or *p* Tolyl (T)), were investigated (designated as, e.g., PG2000 $T_{0.52}$ for a polymer based on a $M_n = 2000$ g mol^{-1} polyglycerol core, 52 % of all OH groups esterified with tolyl groups). An amphiphilic polyethyleneimine amide based on a core of molecular weight $M_n = 4000$ g mol^{-1} amidated to 47 %[21] with palmitic acid (PEI4000 $C15_{0.47}$) was also studied.

Reduction of $Pd(OAc)_2$ in toluene solutions of the amphiphilic polymers, with H_2, with $LiBEt_3H$ ("superhydride") for the polyethyleneimine amides, or by the remaining OH groups of amphiphilic polyglycerol without added reducing agent at 60 °C afforded spherical palladium nanoparticles with sizes in the range of 1 to 9 nm. Somewhat surprisingly, reduction with carbon monoxide resulted in stable toluene solutions of entirely different, much larger geometrically regular particles (Fig. 1).

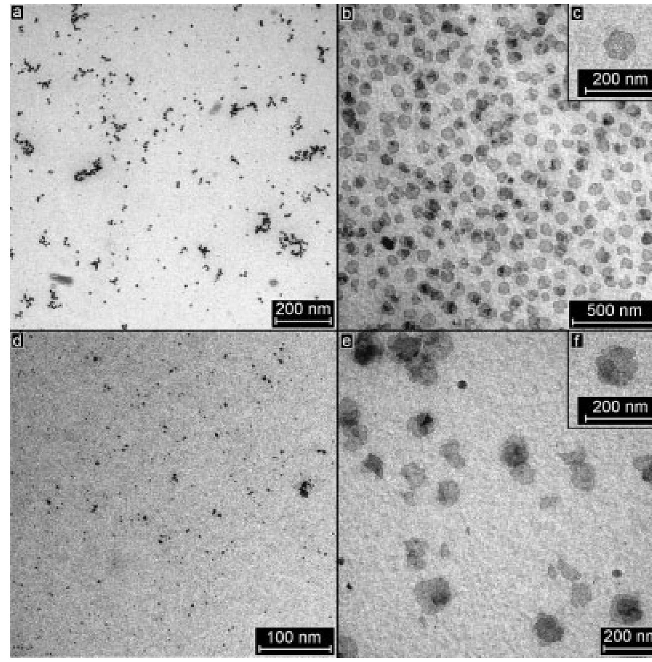

Figure 1. TEM images of palladium particles formed upon a) H_2, b,c) CO reduction of $Pd(OAc)_2$ in the presence of PG4000-$T_{0.62}$, and d) H_2, e,f) CO reduction of $Pd(OAc)_2$ in the presence of PEI4000-$C15_{0.47}$.

Table 1. Particle synthesis: conditions and sizes of the hexagonal particles formed. Particle synthesis by exposing a solution of the amphiphilic polymer and $Pd(OAc)_2$ to CO (1 atm) at room temperature overnight. Particle size as defined in the Experimental section.

No.	Polymer	Polymer conc. [g L^{-1}]	Ratio of polymer/$Pd(OAc)_2$	Particle size [nm]
1	PEI4000-$C15_{0.47}$	1.0	0.33	72 ± 28
2	PG2000-$C15_{0.44}$	10.1	10.1	119 ± 18
3	PG6000-$C15_{0.22}$	10.3	10.2	19 ± 7
4	PG6000-$C15_{0.48}$	10.4	10.3	30 ± 14
5	PG6000-$C15_{0.77}$	10.6	10.6	73 ± 18
6	PG6000-$C15_{1.00}$	10.3	10.2	ca. 400 [a]
7	PG10000-$C15_{0.65}$	9.9	9.6	303 ± 48
8	PG4000-$T_{0.62}$	10.0	18.8	54 ± 16
9	PG4000-$T_{0.62}$	16.6	28.8	59 ± 16
10	PG4000-$T_{0.62}$	16.5	19.1	58 ± 16
11	PG4000-$T_{0.62}$	17.8	10.3	57 ± 12 [b]
12	PG6000-$C15_{0.48}$	10.0	9.9	76 ± 20 (at 15°C)
13	PG6000-$C15_{0.48}$	10.0	9.9	32 ± 12 (at 25°C)
14	PG6000-$C15_{0.48}$	10.0	9.9	33 ± 11 (at 40°C) [c]
15	PG6000-$C15_{0.48}$	10.0	9.9	46 ± 14 (at 25°C) [d]

[a] Largely aggregated. [b] Squares and triangles of up to 10 nm also observed [7e]. [c] Spherical particles also formed, presumably due to the beginning of reduction by the residual OH groups of the polyglycerol. [d] Sample shaken during reduction.

Under suitable conditions, hexagonal platelets with a relatively narrow size distribution and reproducible extensions are formed exclusively (Table 1). The size of these platelets, i.e., the size of their hexagonal faces as defined in the Experimental section, is influenced by various parameters during their synthesis.

For the amphiphilic polyglycerols, the nature of the lipophilic moiety R only has a minor influence on particle shape and size (Table 1, entries 8 to 11 compared to entries 4,5), whereas a higher degree of esterification results in larger platelets (entries 3 6). With a completely esterified polyglycerol, platelets of up to ca. 500 nm are observed.

The molecular weight of the polyglycerol scaffold strongly influences the size of the platelets, albeit not in a simple systematic fashion. Whereas colloids prepared with PG2000

$C15_{0.44}$ have sizes of around 100 nm (entry 2), the size is lowered to 30 nm for colloids generated in the presence of PG6000 $C15_{0.48}$ (entry 4). It can be speculated that the palladium particle formation process is influenced by the flexibility of the scaffold[22] as well as the size of the polymer molecules, which both increase with molecular weight. Applying polymers with a core molecular weight of 10 000 g mol^{-1} results in much larger platelets (entry 7). Experiments with the amphiphilic polyglycerol PG4000 $T_{0.62}$ reveal that the sizes of the resulting particles are not very sensitive towards the metal to polymer ratio or polymer concentration in the range examined (entry 8 to 11), which supports the assumption that the observed influence of the polymer molecular weight and degree of esterification can indeed be traced back to these parameters.

Particles prepared by CO reduction in the presence of amphiphilic polyethyleneimine (PEI) are also hexagons, albeit less regular in comparison to the polyglycerol stabilized platelets. This demonstrates that platelet formation is not unique to the polyether polyol scaffold of the amphiphilic polyglycerols.

The reaction temperature had a strong influence on the results of the platelet synthesis: the platelet size decreased from 76 to 32 nm when the temperature was increased from 15 °C to 25 °C. Raising the temperature to 40 °C did not alter the platelet size further (entries 12 to 14), but additionally resulted in formation of some strongly aggregated structures, presumably due to the beginning of reduction of $Pd(OAc)_2$ by the residual OH groups of polyglycerol.

Reduction with CO in the presence of a partially esterified linear analog of polyglycerol[18b] ($M_n = 1500$ g mol^{-1}, DB 0 %; esterified to 29 % or 54 % with $R = C_{15}H_{31}$) resulted in precipitation of palladium; no stable colloid was obtained. Polyvinyl pyrollidone (PVP) has been investigated thoroughly as a stabilizer for metal colloids.[23] Reduction of $Pd(OAc)_2$ with CO in the presence of PVP in $CHCl_3$ solvent resulted in the formation of irregular platelets and also spherical particles of ca. 2 nm diameter. Apparently the highly branched flexible polymer scaffold in combination with the amphiphilic nature of the polymer is beneficial for regular platelet stabilization.

However, we believe that the structure and nature of the polymer are not the sole keys to shape selectivity, but rather the specific reduction process. For comparison, colloid formation by ligand displacement[4c] from the palladium(0) precursor $[Pd(dba)_2]$ (dba = 1,5 diphenylpenta 1,4 dien 3 one) with carbon monoxide was investigated. Spherical particles of 4 to 6 nm average size are obtained. The colloids are formed within seconds, whereas most of the aforementioned reduction methods occur much more slowly, as evidenced by the gradual darkening of the reaction solutions. Reduction with $LiBEt_3H$ also occurs within seconds; reduction with CO (resulting in hexagonal platelets) requires several hours; and reduction with hydrogen or reduction by the OH groups of polyglycerol without added reducing agent occur overnight. As a general rule, in the formation of any type of particles by reduction processes the rate of reduction will usually strongly affect particle nucleation and growth,[6a] and thus particle size and possibly also shape. With respect to reduction rate, the CO reduction does not stand out from other reductions that yield spherical particles. Rather, the observed unusual shape selectivity is specific to the reduction process of Pd^{II} with CO, in combination with a polymer that apparently adsorbs to certain crystal faces effectively and thus promotes specific crystal growth, as has been suggested for other types of colloid synthesis.[7h,i,9d] It can be speculated that intermediate unstable palladium carbonyl compounds are involved. In the final particles, the polyglycerol is adsorbed by means of its polar, flexible scaffold and the lipophilic moieties provide solubility in apolar media (Fig. 2).

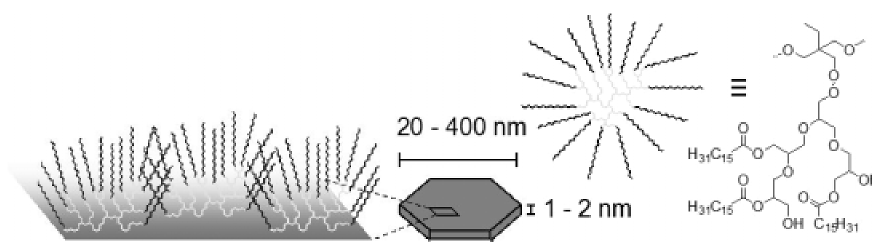

Figure 2. Proposed structure of palladium-platelet polymer hybrids.

Shape and structure of the platelets were further investigated by transmission electron microscopy (TEM). Tilting the sample in the microscope up to the technical limit of 60°, no indication of a significant extension of the nanoplatelets in the third dimension was observed. The thickness of the hexagonal plates was estimated by TEM of mixtures with separately prepared colloids composed of spherical particles of different sizes. For a mixture with spherical particles of 2 nm average diameter, the electron density of the platelets which lay flat on the grid appeared even slightly lower in comparison to the spherical particles. This already indicates that the platelets are approximately 1 to 2 nm thick, corresponding to approximately five to ten layers of atoms.

Clear proof is provided by TEM on a sample, in which some of the platelets have arranged into stacks perpendicular to the grid (see Supporting Information). A platelet thickness of 1.3 nm is observed. Incidentally, it can also be noted that the distance of 5 nm between two platelets is in agreement with a polymer monolayer on each platelet, comparing the distance between platelets with the radius of gyration observed by SANS in solution.[20]

The platelet structure and composition were studied further by high resolution transmission electron microscopy (HRTEM). The relatively high electron beam intensity of the instrument setup used, which exceeds that of regular TEM investigations by two orders of magnitude, unfortunately results in disintegration of the hexagonal platelets to smaller fragments. It can be speculated that the strong electron radiation decomposes the polymer and thus results in a "dewetting" of the particle surface, which induces fragmentation. Notwithstanding, the fragments exhibit lattice plane fringes indicating the crystalline nature of these platelets, even after electron beam induced degradation (Fig. 3). The most commonly ob

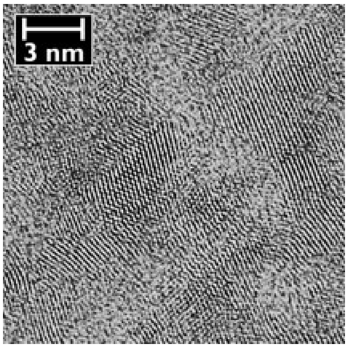

Figure 3. HRTEM image of a part of a hexagonal platelet with lattice plane fringes due to 1/3{422} reflections. Note that platelets have been fragmented under the conditions of the experiment.

served fringe spacing of 0.2361 nm deviates distinctly from the {111} lattice plane spacing (0.2246 nm) of face centered cubic (fcc) palladium metal. Instead, it agrees fairly well with the spacing (0.2382 nm) of fringes due to kinematically forbidden 1/3{422} reflections expected to appear in thin films or platelets with {111} surfaces and rather small thicknesses in the perpendicular direction.[24] The selected area electron diffraction pattern (SAED) of a single platelet confirms this finding (Fig. 4). The observed pattern corresponds to a fcc palladium crystal viewed along a <111> direction, i.e., the large faces of the hexagon platelets correspond to {111}. Besides regular diffraction spots of (220) and (422) type, the SAED pattern is dominated by fractional (forbidden) {422} spots, as indicated in Figure 4. From the diffraction data a lattice constant of $a = 0.387$ nm is calculated, which is in excellent agreement with literature data for palladium ($a = 0.389$ nm).[25]

Sample preparation for electron microscopy involves drying the colloidal solution on the surface of a carbon coated copper grid. Moreover, changes to the sample caused by the electron beam can occur. In the vast literature on colloidal metal particles, it is usually assumed, without further evidence, that the observed structures are not affected and resemble the solution structure. A conceivable formation of Pd nanoparticles only in the electron microscope, e.g., by reduction of traces of residual Pd^{II} compounds, seems very unlikely.[26] The observed platelets of regular shape, narrow size distribution and uniform arrangement with their hexagonal faces parallel to the carbon support cannot be understood in terms of irradiation induced particle formation. Nonewithstanding, further studies by extended X ray absorption fine structure analysis (EXAFS) were carried out to provide confirmation. EXAFS enables the investigation of the particles directly in solution under mild conditions. The spectra confirm the particles to be composed of palladium(0). The spectra are identical to those of palladium foil, and within the accuracy of the experiment (> 90 % palladium(0)) there is no indication of other oxidation states.

Ultrafiltration with solvent stable membranes is a convenient method for recovering a soluble catalyst after a catalytic reaction, and also provides some preliminary insight into the shear sensitivity of the platelet dispersions. Catalytic hydrogenation of cyclohexene was investigated as a model reaction. The catalytic ability of the platelets does not differ dramatically when compared to hydrogenation with spherical colloids stabilized by the same polymers and under otherwise identical conditions, which is expected since hydrogenation is a rather non shape selective reaction. Recovery of the polyglycerol stabilized platelets from the reaction solutions obtained from hydrogenation experiments by ultrafiltration did not result in any change in size or shape.

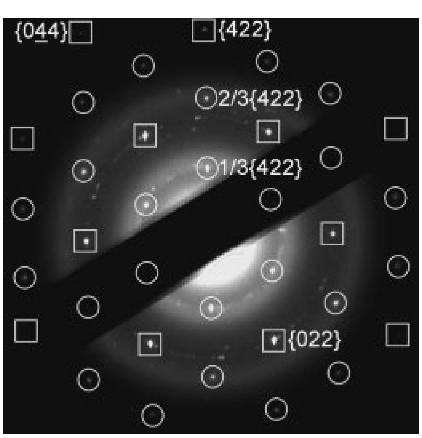

Figure 4. Selected area electron diffraction pattern of a single palladium platelet (prepared with PG6000-C15$_{1.0}$). Regular reflections are marked by open squares, forbidden reflections are marked by circles.

3. Conclusions

In summary, we report on the shape selective synthesis of palladium platelets stabilized by amphiphilic hyperbranched polymers. Very thin (< 10 atomic layers) hexagonal palladium platelets with sizes of fifteen to several hundred nanometers in the other two dimensions are obtained. Remarkably, despite their high aspect ratio, the platelets are also dimensionally stable under some degree of shear. Furthermore the system is exclusively based on readily available reagents.

4. Experimental

Carbon monoxide (99.9 %) supplied by Gerling & Holz and hydrogen (99.999 %) supplied by Messer Griesheim were used as received. Toluene (99.5 %) supplied by Merck was used as received or freshly distilled from sodium under argon in the case of reduction with $LiBEt_3H$. Palladium acetate was supplied by Umicore via Merck; $LiBEt_3H$ supplied by Aldrich as a 1 M solution in tetrahydrofuran was used as received. Hyperbranched polyglycerol and polyethyleneimine were supplied by Hyperpolymers GmbH [16].

Esterification [18] resp. amidation [11] was performed according to literature procedures. In a typical reduction procedure amphiphilic polyglycerol or polyethyleneimine respectively were dissolved together with $Pd(OAc)_2$ in 3 to 20 mL of toluene (dry toluene in case of reduction with $LiBEt_3H$) in a Schlenk tube. In case of H_2 or CO as reducing agent the gas was bubbled through the solution for three minutes before the flask was closed under reducing atmosphere, and stored at room temperature overnight. Reduction by the residual OH groups of the polyglycerol was carried out keeping a solution of polymer and

$Pd(OAc)_2$ at 60 °C over night. Reduction with $LiBEt_3H$ occurred immediately after adding 1 mL of dry toluene incorporating the desired amount of $LiBEt_3H$ to the solution of metal salt and polymer.

The diffusion of CO at room temperature from the gas phase into the solution is sufficiently fast, as shown by two otherwise identical experiments where one flask was shaken overnight (100 rpm) instead of simply storing it overnight (entry 15, Table 1). The resulting diameters are identical within experimental errors.

TEM and SAED investigation were carried out on a LEO 912 Omega apparatus using an acceleration voltage of 120 kV. The particle sizes were determined by measuring the average diameters (average of largest and smallest possible distance between two opposite points on the platelet edge) of ca. 100 platelets and performing a nonlinear least squares fit on the data to a Gaussian model. The center and the half width of the probability distribution function are given in Table 1.

HRTEM investigation was done using a JEM 4010 operating at 400 kV accelerating voltage. Micrographs recorded at optimum imaging conditions (Scherzer focus) were digitized for image processing. Diffractograms of HRTEM images obtained by Fourier transformation were used to measure lattice fringe spacings.

EXAFS Data Collection: Palladium K edge (24 350 eV) EXAFS spectra were measured at the Hamburger Synchrotronstrahlungslabor (Hasylab) Hamburg, Germany, Beamline X1, using a Si(111) double crystal monochromator. The monochromator was detuned to 50 % intensity to avoid effects of higher harmonics present in the X ray beam. The measurements were done in the transmission mode using optimized ion chambers as detectors. To decrease noise scans were made in *k* space and three scans were collected for each sample. Measurements were performed at room temperature.

EXAFS Data Analysis: A Pd foil was measured simultaneously with each sample. The energy was calibrated by assigning the first inflection point of the Pd foil to 24 350 eV. Theoretical reference data were generated in the commercially available program XDAP [27] using FEFF8 [28]. The EXAFS data were analyzed using XDAP [27,29]. During R space fitting the difference file technique [27] was used in order to conclude a good analysis for all contributions in all weightings [30].

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