Colloid Polym Sci 276:769–779 (1998)
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ORIGINAL CONTRIBUTION

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Investigation of polymer-protected noble metal nanoparticles by transmission electron microscopy: control of particle morphology and shape

Received: 2 February 1998
Accepted: 29 May 1998

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Abstract Noble metal nanoparticles were prepared by the in situ reduction of the respective metal salt precursors in the presence of various protective polymers. Transmission electron microscopy (TEM) has been used to determine the particle shapes and morphologies. These are strongly influenced by the reduction methods and conditions chosen, but the choice of the protective polymer is equally important for controlling the particle morphologies and for the stabilization of the colloids. A whole spectrum of nanoparticle morphologies and shapes was obtained, ranging from nanoagglomerates which are nevertheless well-defined and well-stabilized to nanosized single crystals with triangular shape.

Key words Noble metal nanoparticles morphology control – polymer stabilizers – electron microscopy

Introduction

Polymer-protected, nanosized noble metals are receiving increased attention, since they offer a high potential for many technological applications. Gold and silver nanoparticles, for instance, exhibit interesting optical and electronic properties. Depending on the particle size, shape, and agglomeration, gold colloids can adopt a variety of colours, such as yellow, red, violet, or blue [1]. Another important application for colloidal noble metals is in catalysis. Depending on the particle sizes and morphologies very active and selective catalysts can be obtained [2–10].

Polymer-protected noble metal colloids are usually prepared from suitable metal precursors by various in situ reactions, that is, in the presence of the protective polymer. By the choice of the precursors, reduction conditions, and the protective polymer it is possible to control the particle sizes rather well. Block copolymers have shown to be especially promising for this purpose [5, 6, 11–15]. Several other types of polymers have been investigated for their utility to stabilize such colloids, too [2–4, 9, 10]. Often, the choice of the polymer can additionally influence the properties and characteristics of the resulting metal–polymer systems.

Another challenge in colloid chemistry is to control not only the particle sizes, but the particle shapes and morphologies as well, which represents an additional tool to adjust the optical or catalytic properties. Well-stabilized, amorphous nanoagglomerates are highly interesting for catalytic purposes, since they combine high surface areas and catalytic activities with the handling of larger size particles. The controlled growth of nanosized single crystals which expose special crystal planes is equally desirable, since they can provide enhanced selectivities for certain structure-sensitive catalytic reactions.

One very successful concept for size and shape control by polymers is based on the "nanoreactor principle" [16–20], working with the micelles of amphiphilic block copolymers. The metal precursor is accumulated within the micelle core (e.g. by complexation or ion-pair formation with functional groups of the polymer), and the subsequent reduction takes place in this confined reaction environment. The result are colloids incorporated within the micelle core. The micelle core acts as a "nanosized reaction vessel" which limits the growth of the colloidal particles and thus controls their size [16]. In most cases however the hydrophilic blocks, possessing side groups capable of complex formation with the precursor ions, form the micelle cores, and the hydrophobic blocks form the coronas. Therefore, most examples reported so far have been performed in nonpolar, organic media.

For many practical applications however aqueous media are requested, both for environmental and for handling reasons. Incorporation of the colloids into hydrophobic micelle cores is difficult since usually there are no groups present that could form complexes or ion pairs with the precursor ions. By the careful choice of the precursor (e.g. by selecting its hydrophobicity or using steric effects), the reduction conditions, and the solvent composition (e.g. causing come swelling of the micelle core) partial incorporation of metal colloids in such systems was described [21–23]. However, the transfer of the nanoreactor concept to aqeuous systems still remains a challenging task, and further work on specially designed block copolymers is required.

The selection of an appropriate protective polymer can lead to various colloid morphologies by controlling the growth (step 1) and handling of the agglomeration process (step 2). The principle is based on the fact that a polymer can interact with a growing metal nucleus site-specific or in an unspecific way, depending on its functionalization pattern.

Fendler and coworkers have shown, using the seeded crystallization onto Langmuir–Blodgett monolayers as a simple model system, that the shape and orientation of the crystals indeed depend on the composition and density of head groups of the surfactant monolayer film (for a comprehensive review, see ref. [24]). These observation make similar experiments with appropriately functionalized polymers very promising.

First results performed in homogeneous solution prove that similar rules can also be applied in three dimensions: it was indicated that the distance of functional groups along the polymer backbone can influence the crystallization in a specific manner, and special crystal shapes might be expected in dependence of polymer composition (step 1). This interaction does not necessarily stabilize the primary particles, and small agglomerates during the in situ reduction process can be obtained. Depending on the type of polymer, stabilization of all aggregates above a critical size becomes effective again, and further agglomeration and precipitation is prohibited (step 2).

Several options are proposed for such polymeric stabilizer systems:

(1) Amphiphilic block copolymers with a hydrophilic and a hydrophobic block are – for special systems – still an interesting choice since the combination of both destabilizing (e.g. non-hydrophobic) and stabilizing (e.g. hydrophobic) blocks could lead to the desired effect of partial aggregation, simply by adjusting the suitable block types and lengths.

Well-stabilized platinum [21, 22] and rhodium agglomerates have been obtained in the presence of polystyrene-b-poly(ethylene oxide) (PS-b-PEO). It is suggested that the PEO block (as a poor stabilizer for noble metal nanoparticles) leads to the initial agglomeration of the small metal particles which subsequently heteroprecipitate onto the hydrophobic polystyrene micellar core. Block polyelectrolytes are a further promising choice by combining a less-stabilizing, but water soluble ionic block with a micelle inducing hydrophobic block.

(2) Random or alternating copolymers are expected to be suitable, too, when they combine ionic stabilization, ion binding as well as some hydrophobicity. Here, the micellar aggregates are not that well defined, and in some cases, the compartimentized reaction medium is expected to form just during the reaction.

For the purpose of surface stabilization, a number of copolymers between acrylic acid or maleic acid with hydrophobic comonomers, e.g. poly(maleic acid-co-olefin, sodium salt), are commercially availiable, which are to be investigated for the stabilization of noble metal colloids. Here, it is expected that the negatively charged moieties of the polymer just weakly interact with the negatively charged noble metal colloids (charged by counterion adsorption), whereas the hydrophobic parts of the polymers seem to be suited for interaction with and stabilization of the hydrophobic gold colloids, but also induces aggregate formation of the primary polymer chains to a more complex, three-dimensional functionalization pattern. The poly(maleic acid-co-olefin, sodium salt) offers an additional advantage: in ethanol/water mixture as a solvent the gold precursor can be reduced at room temperature in the dark by a "self-reduction" process, presumably by oxidation of the alcohol.

In addition, some other water soluble random copolymers, poly(acrylamide-co-acrylic acid), poly(1-vinylpyrrolidone-co-acrylic acid), poly(1-vinylpyrrolidone-co-vinylacetate), where the separation of hydrophilic and hydrophobic moieties is less pronounced, as well as two amphiphilic homopolymers, poly-2-ethyl-oxazoline and polyoxybutylene, will also be examined.

In some cases where the colloidal stability of the products turns out to be restricted, poly(1-vinyl pyrrolidone) can be used as an additional stabilizer once the colloids were formed. In this way, even those agglomerates can be "preserved" to allow for analysis of their structure.

(3) A third approach to incorporate metal colloids within the micelle core in the presence of water or polar solvents is the use of "double-hydrophilic" block copolymers [23, 25]. Here one of the water soluble blocks carries groups capable of coordinating with the precursor ions, whereas

the second block provides good solubility in water, but just weakly interacts with the metal salt or metal colloid.

Often, these "double-hydrophilic" block copolymers do not form micelles in the respective solvents, but merely loose aggregates. Micelle formation can be induced, however, by the addition of a metal salt precursor which can strongly interact (e.g. by complexation) with part of the core-forming polymer block. Thus, the metal precursor is accumulated within a micelle core and can be expected to remain there after reduction. The stability of the final system, however, will depend very much on the interaction and affinity of the core-forming polymer block with the colloid surface. Previously, it has been found that very stable gold colloids protected by poly(vinyl phosphonic acid) homopolymer could be prepared [26]. For those reasons, a "double-hydrophilic" block copolymer carrying phosphonic acid side groups in one block and polyethyleneoxide in the other, PEO-b-phosphonated PMA block copolymer, was chosen to be included in this examination for the preparation of gold and platinum colloids. Since the phosphonic acid ligands are obviously also advantageous to support the catalytic activity of colloids [9], formation of palladium or platinum colloids will also be investigated.

Formation of small single noble metal crystals requires a certain "controlled growth", also the reduction methods and conditions are highly important. It has been observed, for instance, that the use of certain polyacids (in combination with the reduction of the metal precursor by a slower reduction method, such as the UV photoreduction) leads to the preferred formation of gold single crystals in the nanometer size range [17]. It is obvious that for crystal growth control slower reduction methods are preferable to faster ones.

Simply by the variation of the reducing agent a wide variety of particle shapes and morphologies can be obtained for certain polymers. Therefore, reduction conditions will be varied in a systematic fashion for some polymers to explore the influence of this parameter in context with the different polymer patterns applied.

UV–VIS spectroscopy which sensitively reacts to primary particle size allows a fast screening and classification of the resulting colloid morphologies. The shapes, morphologies and sizes of both single crystals and agglomerates will be investigated by transmission electron microscopy (TEM).

Experimental

Chemicals and reagents

Hydrazine hydrate ($N_2H_4 \cdot H_2O$), gold chloride ($AuCl_3$), tetrachloroauric acid $HAuCl_4$, potassium borohydride KBH_4, dihydrogen hexachloroplatinate H_2PtCl_6, rhodium acetate $Rh(CH_3COO)_3$, poly(maleic acid-co-olefin, sodium salt) (average molecular weight $M_w \sim 12\,000$), poly(styrene-alt-maleic acid, sodium salt) (M_w 120 000), poly(1-vinyl pyrrolidone), poly(acrylamide-co-acrylic acid) (M_w 200 000), poly(2-ethyl-2-oxazoline) (M_w 200 000), poly(vinyl pyrrolidone-co-vinyl acetate) (60 : 40 (mol); $M_w \sim 50\,000$), and poly(vinyl pyrrolidone-co-acrylic acid) (75 : 25 (wt); $M_w \sim 96\,000$) were obtained from Aldrich. Poly(acrylic acid-co-maleic acid) (Sokalan CP 45; M_w 70 000) and poly(C_{12} olefin-co-maleic acid anhydride) (ZK 396/122; M_w 5000) were obtained from BASF. Polystyrene-b-poly ethylene oxide (PS-b-PEO; M_n of PS 29 800; M_n of PEO 8400; M_w/M_n 1.03) was purchased from Polymer Source, poly(1,4-oxybutylene) from Polysciences.

The block copolymer PEO-phosphonated PMAA (partial phosphonation) was synthesized according to ref. [25]. For steric reasons only partial phosphonation was achieved (^{31}P NMR: 21% monophos.). It has been dialyzed against water for five days (Spectra/Pol Membrane, MWCO 1000, wetted in 0.1% sodium azide).

Colloid preparation

Gold colloids in the presence of Sokolan-type copolymer by "self-reduction"

An ethanolic solution of the gold precursor $HAuCl_4$ was mixed with an aqueous solution containing the Sokalan-type copolymers (poly(maleic acid-co-olefin, sodium salt), poly(styrene-alt-maleic acid, sodium salt), poly(acrylic acid-co-maleic acid), or poly(C_{12} olefin-co-maleic acid anhydride)) in a mass ratio of polymer: Au = 25 : 1 to result in a solvent mixture ethanol : water = 1 : 1, v/v (6.8×10^{-4} M $HAuCl_4$). No additional reducing agent was added. For poly(maleic acid-co-olefin, sodium salt) the gold colloids were formed within one to five minutes which was observed by the appearance of a deep violet or blue colour. In some cases an aqueous solution of poly(1-vinyl pyrrolidone) has been added to the gold colloids once they were formed for additional stabilization. Application of pure water as a solvent under similar conditions does not result in colloid formation.

Noble metal colloids by reduction with potassium borohydride or hydrazine hydrate

About a twofold excess of KBH_4 has been freshly dissolved in water and was rapidly added at room temperature to the stirred solution containing the metal precursors (6.8×10^{-4} M) and the protective polymer in a mass ratio of polymer : metal salt = 25 : 1. Alternatively,

$N_2H_4 \times H_2O$ was similarily added with a syringe. An immediate color change was observed in both cases thus indicating the spontaneous formation of the colloids within seconds.

Gold colloids prepared by the photoreduction

The stirred and water-cooled solution (6.8×10^{-4} M; ethanol:water = 1:1, v/v) containing the gold precursor $HAuCl_4$ and the polymers in a mass ratio of polymer : gold = 25:1 was irradiated with a Hanovia Ultraviolet Quartz Lamp for 45 min in presence of oxygen. After irradiation, all samples have turned deeply violet.

Gold colloids in the presence of poly(acrylamide-co-acrylic acid) by "self-reduction"

The standard solution (6.8×10^{-4} M:ethanol : water = 1 : 1, v/v) containing $HAuCl_4$ and the copolymer in a mass ratio of copolymer:Au = 25 : 1 was reduced by refluxing for one hour under stirring. A purple-violet colloidal solution is obtained which starts forming a "gelly" precipitate after about two hours.

All glassware has been cleaned with aqua regia before use.

Characterization

UV–VIS spectra (10 mm pathlength cuvettes) of the samples were taken with a Milton Roy Spectronic 3000 Array instrument and a Kontron UV-IKON 931 instrument (operating over a range between 190 and 900 nm) immediately after the preparation of the metal colloids and for some selected species after fixed times to test the stability. UV–VIS spectroscopy has been also used to test the completeness of the "self-reduction" processes.

Transmission electron micrographs were taken with a JEOL-100 CX II transmission electron microscope (operated at 80 kV) or with a Zeiss 912 Ω (100 kV) in order to obtain the shapes, morphologies, and sizes of the metal colloids. The samples were prepared by placing a drop of the colloid on a formvar/carbon-coated copper grid and letting the solvent evaporate. For examination of the gelled sample, a grid was gently pressed against the gel and left to dry.

Results and discussion

Already observation by the naked eye indicates that the formed colloids are peculiar, as compared with the reduction of gold salts stabilized with low molecular weight component: many of the gold colloids formed are exhibit an unusual blue and violet colour. These colours are usually known from gold sols close to instability or agglomeration, but most of the polymer protected systems are stable for months.

Two of the corresponding UV–VIS spectra for poly(maleic-acid-co-olefin,sodium salt), reduced by the self reduction process as well as with KBH_4, are shown in Fig. 1a, and compared with conventional spectra, as obtained by the PEO-phosPMMA copolymer (Fig. 1b).

It is seen that both spectra in Fig. 1a are rather unstructured: the self-reduction results in a broad peak, typical for aggregates of larger gold particles. Reduction with KBH_4 results in the appearance of a band at about 510 nm, typical for small gold colloids, but the spectra exhibit at the same time a very unusual strong absorption in the near IR-region which is just touched within the presented spectral range. Such low energy transitions are expected for an intimate electronic coupling in an array of single metal colloids where the wavefunctions extend across the surface of each particle [27], i.e. we expect this sample to consist of a tightly packed ensemble of small colloids. For comparison, the spectral behavior of stable, isolated gold particles is shown in Fig. 1b: the reduction of gold salt in PEO-b-phosPMA with hydrazine results in larger particles (narrow plasmon band with a strong absorption maximum at 560 nm, corresponding to a deep red colour) whereas fast reduction gives a orange-yellow solution with a much lower extinction and a slight shoulder in the spectrum at about 520 nm, typical for the coexistence of gold clusters (being composed of just a few atoms) and very small gold colloids.

For both polymers, the stronger reducing agent KBH_4 results in faster nucleation and creates small primary particles, whereas slower reduction techniques give larger particles. In addition, PEO-b-phosPMA is obviously able to stabilize the primary particles, whereas controlled aggregation towards larger entities takes place in case of the poly(maleic-acid-co-olefin, sodium salt).

This interpretation of the UV-spectra is also supported by transmission electron microscopy.

The resulting particle morphology of a borohydride reduction is shown for gold in poly(acrylamide-co-acrylic acid) (Fig. 2a), whereas the result of the self-reduction is depicted for poly(maleic acid-co-olefin, sodium salt) (Fig. 2b). Both morphologies are however typical for the reduction method combined with a whole variety of different statistical copolymers. From higher resolution micrographs, one can estimate that for the borohydride reduction the primary particles possess an average diameter of ca. 2 nm, whereas alcohol reduction gives a size of ca. 12 nm. The aggregation to controlled entities for both

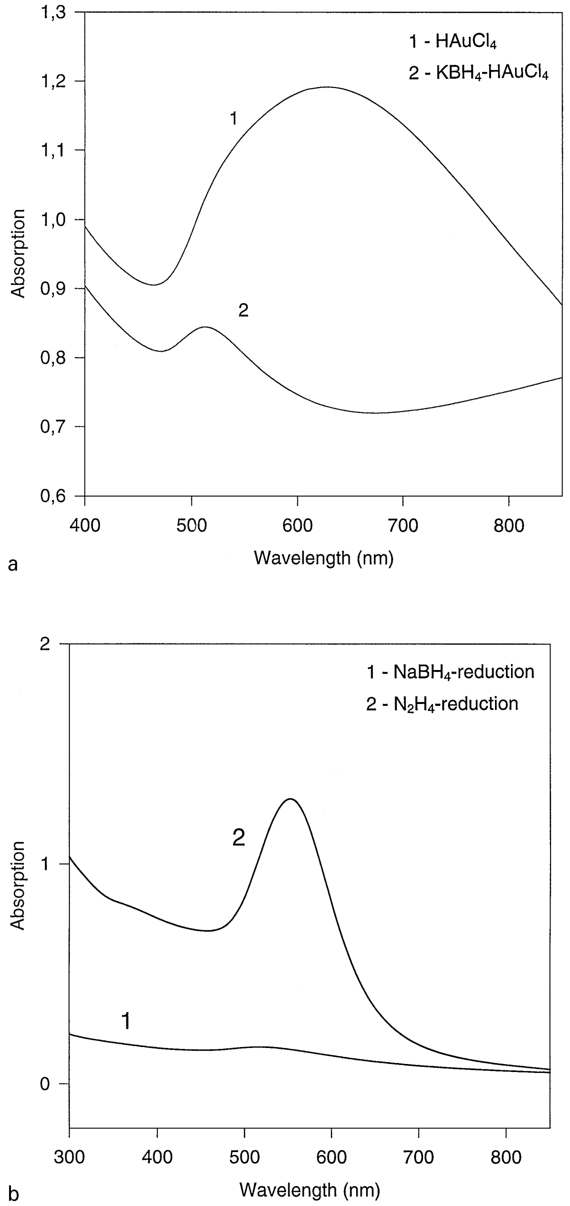

Fig. 1 (a, b) UV–Vis spectra of four different samples of colloidal gold colloid: (a) examples for colloidal aggregates, stabilized with poly(maleic acid-co-olefin, sodium salt), reduced by boiling in alcohol (1) and by addition of KBH_4 (2); (b) well stabilized primary particles in PEO-b-phosPMMA, reduced by addition of KBH_4 (1) or by hydrazine (2)

particle sizes in case of the statistical copolymers of the Sokolan type is also nicely visualized.

It is stressed that these observations are in good agreement with the classical work of Turkevich et al. [28] who varied the reduction conditions of gold sols over a wide range (without polymeric stabilizers) and found similar relations between nucleation rates and particle morphologies. With respect to this point, growing colloids with and without polymeric surfactants behave in a very similar fashion.

The secondary aggegation process towards limited aggregates can be avoided by employment of more efficient stabilizers, for instance the double hydrophilic block copolymers. This was already discussed in context with the UV-spectra shown in Fig. 1b, but is graphically illustrated in Fig. 2c and d. Reduction of gold in PEO-b-phosPMA by addition of KBH_4 results in extremely small particles which group during film formation in liquid-like droplets (Fig. 2c) whereas reduction with hydrazine in the presence of the same polymer results in stable, isolated single gold nanocrystals with a diameter of ca. 20 nm (Fig. 2d).

All other polymer/salt/reducing agent combinations have been characterized in a similar fashion; a summary of these results is given in Table 1.

For the Sokolan-type polymers, it turned out that no noticeable change is found with respect to the color and the UV–VIS spectra of the colloids whether the samples are stirred at ambient light or in the dark. Also, once the colloid is formed the addition of a further polymer (here PVP) in water or the simple addition of more water does not give a noticeable change in color or the UV–VIS spectrum as well, even though the polymer content and dilution is increased. Thus, the addition of another polymer can be used to provide an additional and improved stabilization of the colloids.

In addition to poly(maleic-acid-co-olefin, sodium salt), some other Sokalan-type copolymers have been investigated as well. The results for these experiments are also listed in Table 1. The comparably hydrophobic poly(C_{12}-olefin-co-maleic anhydride) forms a very turbid suspension in ethanol : water (1 : 1, v/v) mixture. For this copolymer the “self-reduction” at room temperature (in the dark, without any further reducing agent) is very fast, and a lilac-colored suspension is obtained. No UV–VIS spectrum was taken because of its turbidity. Poly(styrene-alt-maleic acid, sodium salt) does not lead to “self-reduction” of the gold precursor at room temperature, even though this copolymer is very similar to poly(maleic acid-co-olefin, sodium salt). Thus, it seems that the hydrophobic “olefin” part of the poly(maleic acid-co-olefin, sodium salt) copolymer influences the reducibility of the gold precursor. For poly(acrylic acid-co-maleic acid), which does not contain strong hydrophobic moieties, the self-reduction at room temperature is remarkably slowed down. Stirring in the dark and at room temperature for several days merely results in a very light blue color.

It is seen that application of a faster reducing agent in combination with a whole set of polymers results in the formation of controlled colloid aggregates. In all cases, the

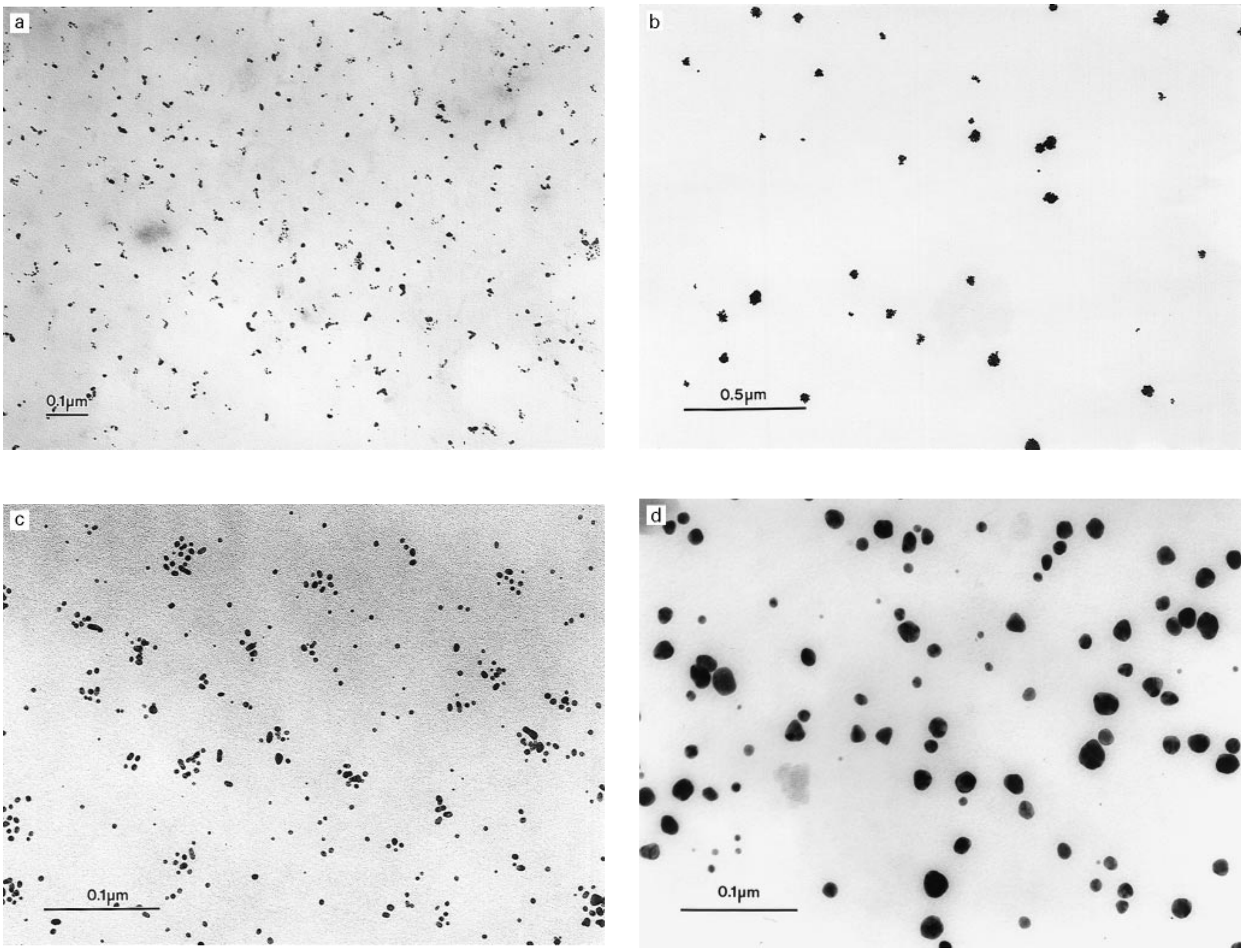

Fig. 2 (a–d) Transmission electron micrographs of the four different morphologies of colloids and colloidal aggregates which were characterized by UV–Vis in Fig. 1: (a) gold nanoparticles in poly(acrylamide-co-acrylic acid), KBH_4-reduction and (b) reduced by boiling in alcohol. Reduction of gold in PEO-b-phosPMMA by addition of KBH_4 results in extremely small particles which are grouped in liquid-like droplets whereas reduction with hydrazine in the presence of the same polymer results in stable single gold nanocrystals with a diameter of ca. 20 nm

small primary particles aggregate to mesosized objects with overall sizes between 20 and 50 nm. In addition to the "simple" structures shown in Fig. 2a–d, four other morphologies are found which are depicted in Fig. 3a–d.

Application of the very slow reduction by UV results for a number of polymers in the formation of single crystals, which however do not grow to a close-to spherical object (as seen in Fig. 2c, but also typically obtained for low molecular weight stabilizers as citric acid or thiol-derivatives), but form platelet-like structures with a strong bimodality of the UV plasmon resonance (thin platelets). A nice example is depicted in Fig. 3a where stabilization with poly(1-vinyl pyrrolidone-co-vinyl acetate) results in the formation of small triangles and truncated hexagons. Particularily nice crystals are also found for poly(oxybutylene) where the reduction almost exclusively resulted in single-crystalline triangles. For the other polymers and UV reduction, trunkated triangles and hexagons are also found, so platelet-like objects are the dominant colloid morphology.

Obviously, diverse polymers stabilize the (1 1 1)-surface of the cubic gold crystals, which therefore preferentially grow along the other crystal planes (the slowest growing crystal surface is always exposed). This is a first indication that functional polymers can influence the crystal growth for sufficiently slow growth conditions.

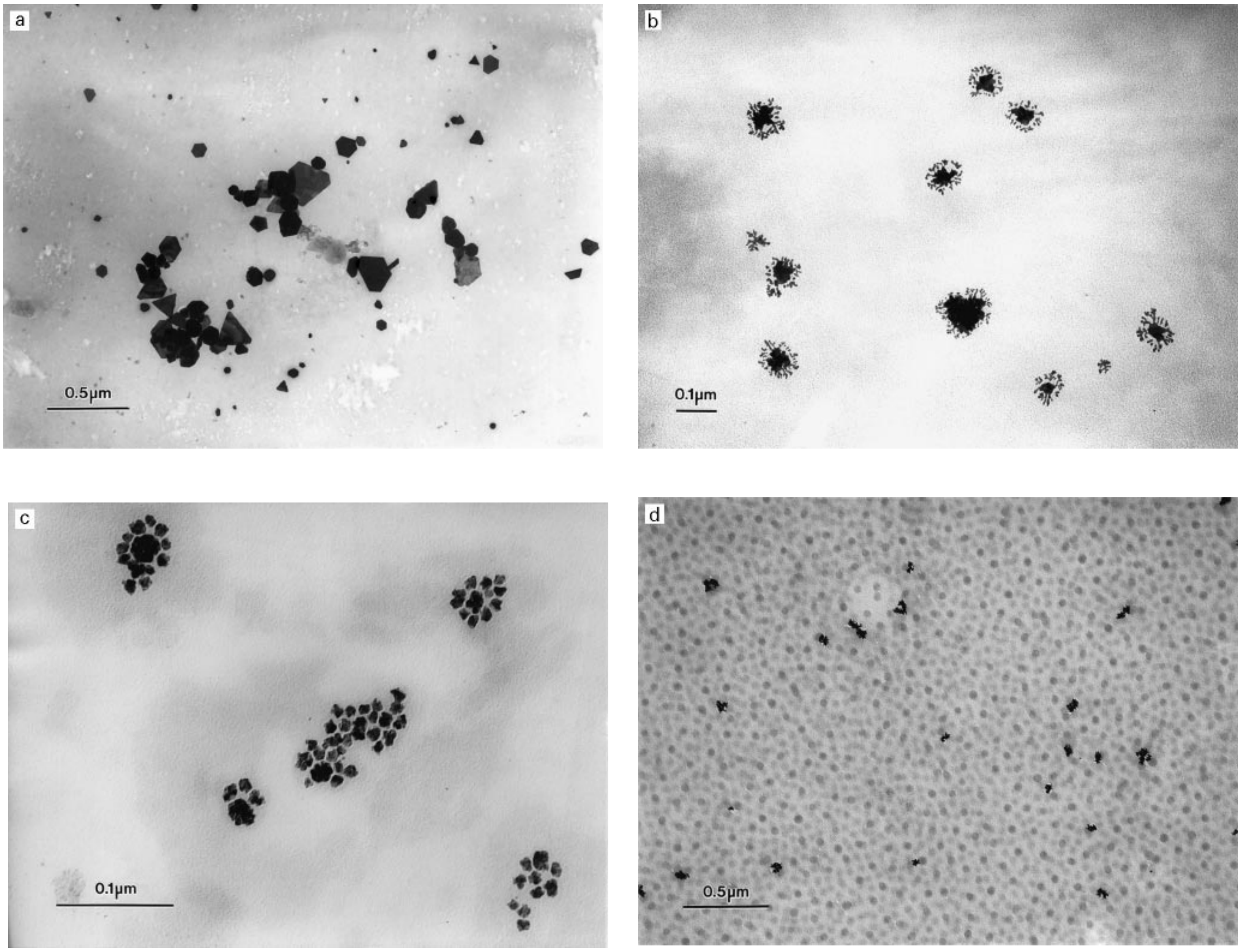

Fig. 3 (a–d) Transmission electron micrographs of some selected special colloid morphologies; (a) crystalline gold platelets in poly(acrylamide-co-acrylic acid), UV-reduction; (b) dendritic gold nanoparticles via alcohol reduction in the same polymer, (acrylamide-co-acrylic acid); (c) boulder like platinum colloids, synthesized by sequestrial reduction of H_2PtCl_6 with hydrazine and KBH_4 in the presence of PEO-b-phosPMA double hydrophilic block copolymers. The boulders are always arranged in small groups, where smaller particles surround the big ones. (d) Stable clusters of primary rhodium nanoparticles, obtained by KBH_4-reduction in the presence of PS-b-PEO micelles. It is seen that the block copolymer micelles are attracted by the colloid aggregates and stabilize the noble metal clusters as micellar entities

The morphology shown in Fig. 3b belongs to the aggregate type structures again and is obtained by reduction in ethanol/water in presence of the anionic acrylamide copolymer, poly(acrylamide-co-acrylic acid). Here, the clusters are not randomly organized, but exhibit a pronounced dendritic, fractal like growth. The fact that the UV radiation in presence of gold salts also produces a gel shows the polymer is presumably oxidized in proximity of the metal surface, which adds a steric or elastic component to the growth control. Similar dendritic gold colloids were already described for the reduction of gold salts in microgels [29]. This observation, occurring in the present contribution as an unplanned side reaction, shows that future work should consider the systematic variation of cross-linking the polymer templates, too.

It is worth mentioning that photoreduction by UV irradiation with the same polymer under otherwise same conditions gives again the platelet morphology, whereas reduction with KBH_4 results in the controlled aggregation process described in Fig. 2a.

Figure 3c shows the unexpected boulder like morphology of platinum colloids, synthesized in the presence of PEO-b-phosPMA double hydrophilic block copolymers. Here, the H_2PtCl_6 precursor was at first reduced with hydrazine; since this reduction step was incomplete, the remainder of Pt-salt was reduced by a second addition of

Table 1 UV–VIS spectroscopic and TEM data for metal nanoparticle polymer samples

Sample code	Protective polymer, preparation	Color	UV–Vis[a) λ_{max} (nm) [Absorption][b)	Remarks	Morphology
Au 1	Poly(maleic acid-co-olefin, sodium salt); $HAuCl_4$; "self-reduction"[c)	Deep blue, clear	Broad ~500–850 maximum: 596	Stable for months	Stabilized nanoagglomerates of larger particles (Fig. 2a)
Au 2	Poly(maleic acid-co-olefin, sodium salt); $HAuCl_4$; KBH_4 reduction[c)	Deep violet, clear	Broad ~518	Stable for months	Stabilized nanoagglomerates of smaller particles (Fig. 2b)
Au 3	Poly(maleic acid-co-olefin, sodium salt); $HAuCl_4$; solvent: pure H_2O no EtOH; stirred at RT in the dark	Colorless No color change	No UV–VIS taken	Control experiement, no colloids produced	–
Au 4	Poly(maleic acid-co-olefin, sodium salt); $HAuCl_4$; PVP (in H_2O) added after reduction; stirred at RT	Deep blue, clear	Broad ~500–850	Stable for months	Stabilized nanoagglomerates of large particles
Au 5	Poly(acrylic acid-co-maleic acid), M_w 70 000; $HAuCl_4$; "self-reduction"[c)	Light blue (after 4 days)	Shoulder ~500–800	No complete reduction	–
Au 6	Poly(C_{12}olefin-co-maleic anhydride); M_w 5000; $HAuCl_4$; "self-reduction"[c)	Milky "lilac"	Turbid	Sedimentation	Very large aggregates
Pt 2	PEO-phosphonated PMA; H_2PtCl_6; reduced with N_2H_4 and $NaBH_4$	Brown	212.0 [2.2]	Stable for months	Boulders (Fig. 3c)
Pt 3	PEO-phosphonated PMA; H_2PtCl_6; reduction by $NaBH_4$	Light brown	194.0 [1.26] +shoulder	Superposition Pt colloid and polymer; Stable for months	Clusters and small colloids liquid like droplets
Au 9	PEO-phosphonated PMA; $AuCl_3$; reduction by $NaBH_4$	Brownish-violet	193.0 [1.4] +shoulder (broad peak) ~520 nm [~0.2]	Gold colloid Stable for months	Clusters and small colloids liquid like droplets (Fig. 2c)
Au 10	PEO-phosphonated PMA; $AuCl_3$; reduction by N_2H_4	Red	206.0 [2.2] 551.0 [0.29] two defined peaks	Polymer gold colloid; Stable for months	Big, isolated colloids (Fig. 2d)
Pt 4	PS-b-PEO, H_2PtCl_6; reduction by KBH_4	Brown, clear	No peak	Stable for months	Small stabilized nanoagglomerates
Rh 1	PS-b-PEO, $Rh(CH_3COO)_3$; reduction by KBH_4	Dark brown, clear	No UV–VIS taken	Stable for months	Small stabilized nanoagglomerates (Fig. 3d)
Au 11	Poly(acrylamide-co-acrylic acid); $HAuCl_4$; reduction by KBH_4	Violet-purple, clear	Broad 523.0	Stable for months	Small primary particles; close-to-spherical and elongated particles; controlled aggregation
Au 12	Poly(acrylamide-co-acrylic acid); $HAuCl_4$; UV photoreduction	Violet, transparent	No UV–VIS taken	Gel formation[d)	Nanosized single crystals (platelet) (Fig. 3a)
Au 13	Poly(acrylamide-co-acrylic acid); $HAuCl_4$; alcohol reduction	Purple-violet, slightly turbid	No UV–VIS taken	After about 2 h formation of a "gelly" precipitate ("strings")	Dendritic clusters (Fig. 3b)
Au 14	Poly(1,4-oxybutylene), M_w 650; $HAuCl_4$; reduction by KBH_4	Dark violet, clear	Broad/shoulder ~480–600 Maximum ~539	Precipitation after several days	Badly stabilized agglomerates

Au 15	Poly(1,4-oxybutylene), M_w 650; $HAuCl_4$; UV photoreduction	Reddish-yellow, blueish when held against light	No UV–VIS taken	Starting precipitation after some days	Single crystals (triangles)
Au 16	Poly(2-ethyl-2-oxazoline), M_w 200 000; $HAuCl_4$; UV photoreduction	Purple	No UV–VIS taken	Starting precipitation after some days	Small amorphous particles
Au 17	Poly(1-vinyl pyrrolidone-co-acrylic acid); $HAuCl_4$; UV photoreduction	Red/purple, turbid, clear when held against light	Broad 549.0	Stable for weeks	Single crystals, in coexistence with amorphous particles
Au 18	Poly(1-vinyl pyrrolidone), M_w 360 000; $HAuCl_4$; UV photoreduction	Red	No UV–VIS taken	Stable for months	Amorphous nanoparticles
Au 19	Poly(1-vinyl pyrrolidone-co-vinyl acetate), $HAuCl_4$; UV photoreduction	Purple-violet	Broad 554.9	Stable for 1–2 days	Single crystals
Au 23	Poly(ethylene oxide), M_w 200 000; $HAuCl_4$; reduction by KBH_4	Dark violet, clear	Broad ~470–>600	Precipitation after 2 days	Large agglomerates
Au 24	Poly(ethylene oxide), M_w 200 000; $HAuCl_4$; UV photoreduction	Purple, turbid	No UV–VIS taken	Stable for few days	Disorganized
Au 25	Poly(ethylene oxide), M_w 900 000; $HAuCl_4$; UV photoreduction	Purple, turbid	No UV–VIS taken	Stble for few days	Disorganized
Au 26	Poly(vinyl phosphonic acid); $HAuCl_4$; UV photoreduction	Deep red-purple	No UV–VIS taken	Stable for several days	Single crystals
Au 27	Poly(styrene sulfonic acid); $HAuCl_4$; UV photoreduction	Red	Broad 549.0	Stable for weeks	Single crystals
Au 28	Poly(2-acrylamido-2-methyl-1-propane sulfonic acid); $HAuCl_4$; UV photoreduction	Red	Broad 539.1	Stable for weeks	Single crystals
Au 29	Poly(acrylic acid); $HAuCl_4$; UV photoreduction	Purple	No UV–VIS taken	Unstable; precipitate after one day	Disorganized agglomerates
Au 30	Poly(2-hydroxypropylmethacrylate); $HAuCl_4$; KBH_4 reduction	Deep wine red/ purple, clear	Broad ~490–600	Stable for several months	Separate spherical and elongated (“fused”) particles
Au 31	Poly(2-hydroxyethylmethacrylate); $HAuCl_4$; KBH_4 reduction	Deep purple/ violet	Broad ~490–600 max. ~535	Stable for several months	Separate spherical and elongated (“fused”) particles

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[a] UV–VIS data of freshly prepared colloids.

[b] As revealed from TEM.

[c] Solvent: ethanol : water = 1 : 1, v/v; no additional reducing agent; no additional poly(1-vinyl pyrrolidone) added; mass ratio: polymer : gold = 25 : 1.

[d] In addition, some violet colloidal dispersion was formed. For TEM investigation of the gel, this dispersion was filtered off and the TEM grid gently pressed against the gel.

KBH_4.The boulders are always arranged in small groups, where smaller particles surround the big ones. The distance between two neighbouring particles is about constant and presumably corresponds to the thickness of the two adsorption layers of polymer (ca. 3 nm, as taken from TEM). The reason for this special superstructure formation is still unknown to us.

Well-stabilized platinum and rhodium nanoagglomerates were also synthesized by reduction with KBH_4, for instance in the presence of PS-b-PEO block copolymers. Figure 3d shows a micrograph for the rhodium particles. It is seen that the hydrophobic polystyrene cores seems to interact and stabilize the rhodium nanoagglomerates as micellar entities, i.e. each rhodium cluster is closely surrounded by a small number of micelles which preserve a low sedimentation coefficient and support colloidal solution. Such micrographs seem to confirm the proposed principle of initial agglomeration (partially caused by the poor stabilizer for noble metal colloids, PEO, and the fast reduction method causing initially very small particles) and subsequent stabilization by a hydrophobic polymer part [21, 22]. For both noble metals the colloids were stable and clear for several months, and precipitation of the metal did not occur. Such limited aggregates with their high interface area and the metal colloids being not buried in the micelle core are very interesting for catalytic purposes, such as hydrogenation or oxydation reactions, and the preparation of conductive films.

At the end, we want to underline that variation of the water soluble polymer, as partly performed in Table 1, includes a variety of further options, relation to the type of functionality and functionalization density. Sulfonic-acid and phosphonic-acid side groups, for instance, are expected to be especially suited for the stabilization of noble metal colloids due to the softer sulfur and phosphorus containing groups which are already known to form stable complexes with gold and show a higher affinity towards gold surfaces [1]. This was performed by means of samples Au 26–Au 28, where large single crystal platelets were obtained. In addition, such electron interacting surface groups are expected to modify both the spectroscopic as well as the catalytic behavior of such polymer protected colloids.

It is also seen that the distance of such acidic groups along the polymer backbone might be an important structure and stability determining factor. This is shown by comparing samples Au17, Au18 and Au29. The random copolymer poly(1-vinyl pyrrolidone-co-acrylic acid) leads to partial formation of well defined single crystals, whereas both pure poly(acrylic acid) as well as poly(1-vinyl pyrrolidone) did not show any pronounced tendency of forming organized products under the respective reaction method and conditions. The problem of controlling colloid morphologies by appropriate patterning of the polymeric stabilizer however requires more detailed examination and will be part of forthcoming work.

Conclusions

It was shown by TEM that a whole number of different colloid morphologies can be adressed by appropriate combination of polymeric stabilizer and reduction method. Variation of the polymeric stabilizer includes adjustment of the hydrophobic/hydrophilic balance, type and density of different functional groups as well as their distribution along the chains, i.e. block copolymers as well as statistical polymers have been applied.

Typical for one set of polymer stabilizers, mostly copolymers, is the controlled formation of stabilized nanoagglomerates, which are expected to be interesting for many technological applications. This morphology is characterized by a high interface area, the handling of the larger aggregates, and place additional electronic transitions to the chemists disposal, as seen in the UV-spectra. Often, such agglomerated nanoparticles tend to agglomerate further and finally precipitate. A whole number of the colloidal aggregates presented in this contribution are however stable for several months.

It is proposed that the polymer becomes an efficient stabilizer just for larger size entities, which might be due to the lower interface area involved, but can also be due to some steric hinderance caused by the polymeric nature. It is even possible that the initial approach of the small primary particles is induced by the polymer, binding to more than one particle, which induces aggregation by bridging.

Another interesting class of colloids generated by the very slow UV-reduction are very large, but thin platelet-like gold nanocrystals with triangular or truncated hexagonal shape, the size and homogeneity of which also crucially depends on the type of the protective polymer. The results seem to imply that the choice of the side groups or certain atoms along the polymer backbone and their distance enables the construction of a chemical “pattern”, which acts as suitable nucleation site or interact with special crystal planes of the growing species. This is in good agreement with the work of Fendler and coworkers on the controlled two-dimensional crystallization on mixed Langmuir–Blodgett films [24].

The layout of such patterns, along with requirements concerning the interactions and affinities of these side groups towards the colloid surface as well as the demanded colloidal stability, are regarded as a key for the generation and structural handling of colloidal, nanosized metal objects.

Acknowledgements We would like to thank Professor R. Morris, Department of Cell Biology, Neurobiology and Anatomy, University of Cincinnati, for providing access to his transmission electron microscopy facility, and Professor M. Wilson, Department of Chemistry, University of Cincinnati for his help in obtaining UV-VIS spectra.

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