Systematic Control of Size and Morphology in the Synthesis of Gold Nanoparticles

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The synthesis of gold nanoparticles (Au NPs) capped by poly(1-vinylpyrrolidin-2-one) (PVP, average $M_w = 10 000$ kDa) yields moderately dispersed (6–8.5 nm) product with limited morphological control while larger NPs (15–20 nm) are reliably prepared using trisodium citrate (Na$_3$Cit) as a reductant/capping agent. Excellent size control in the intermediate 10 nm regime is achieved by hybridizing these methodologies, with highly monodisperse, polycrystalline Au NPs forming. For a Na$_3$Cit:PVP:Au ratio of 3.5:3.5:1, anisotropic NPs with an aspect ratio of 1.8:1 suggest the systematic agglomeration of NP pairs. Enhanced control of NP morphology is allowed by the 1,2-tetradecanediol reduction of Au$_{III}$ in the presence of straight chain, molecular anti-agglomerants. Last, ligand substitution is used to controllably grow preformed Au seeds. In spite of the extended growth phase used, the replacement of phosphate by 1-pentadecylamine affords highly monodisperse, cuboidal NPs containing a single clearly visible twinning plane. The allowance of particle growth parallel to this close-packed plane explains the remarkable particle morphology.

1. Introduction

Since the formative work of Haruta and Hutchings,[11] the importance of gold nanoparticles (Au NPs) in catalysis has become well established. Although sub-5 nm NPs are typically required for catalysis, the non-cytotoxic nature, intense light scattering ability and ease of bioconjugation of larger Au NPs suggest applications in cellular imaging.[2] Meanwhile, the low susceptibility of Au NPs to photobleaching combined with their biocompatibility and enhanced accessibility to and retention by cancer cells[3] make them ideal photothermal coupling agents.[4] Applications in photothermal drug delivery based on the conjugation of drug molecules to Au have also been developed recently.[5] However, bioapplications have been hampered by the discontinuity in the size regimes in which Au NPs can be readily prepared. In spite of the extensive literature pertaining to the synthesis of gold nanoparticles, the challenge of producing narrowly dispersed nanoparticles in the ca. 10 nm range remains non-trivial.[6]

Various chemical methods exist for preparing Au NPs. The reproducible reduction of [AuCl$_4$]$^{-}$ was reported by Turkevich to give 20 nm particles.[7] Developed methods now fall into four categories: 1) borohydride reduction of [AuCl$_4$]$^{-}$ in the presence of an alkane thiol in a water-toluene system rendering sub-5 nm particles[8] (for variants on this method see ref.[9a,9b] 2) forming a microemulsion or micelles in two-phase systems containing surfactants, the concentration of which control particle size;[9] 3) reduction-by-solvent of [AuCl$_4$]$^{-}$ in hot alcohol in the presence of a polymer to coordinate gold ions prior to reduction giving 5–400 nm particles;[10] 4) reduction by trisodium citrate (Na$_3$Cit) in water affording ca. 20 nm particles.[11] The growth of preformed particles by ligand substitution has also been developed, with the conversion of PPh$_3$-capped nanoparticles (1.4 ± 0.4 nm) to their 1-pentadecylamine-capped analogues ($\lesssim$7.2 ± 1.2 nm) having been reported.[12] Similar advances have been reported recently with the Na$_3$Cit reduction of gold ions, with the formation of Au NPs in the regime 20–40 nm reported to be pH dependent.[13]

In spite of efforts, it is clear that the controlled and tunable fabrication of Au NPs ca. 10 nm in diameter, which represents the transition from catalytic particles to plasmonic crystals, has not been well explored.[6] More generally, the controlled variation of NP size as a function of synthetic conditions has not been fully elucidated or, where systematic size variation has been noted, it has not hitherto been commensurate with the retention of size distribution and/or morphology. In this work, we fabricate narrowly dispersed Au nanoparticles with mean particle sizes (MPs) of ca. 3–20 nm. Initial reduction by sodium citrate or in the presence of poly(1-vinylpyrrolidin-2-one) (PVP)[14] is superseded by a hybrid technique. The combination of steric stabilization from the PVP and electrostatic stabilization from the citrate ions prevents agglomeration and allows for the formation of narrowly dispersed NPs with MPs in the 9–14 nm range, with sizes controlled by the precise PVP: citrate ratio. Poor morphology suggests a limited growth phase, which is overcome by the use of 1,2-tetradecane diol in conjunction with straight-chain molecular capping agents.

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to yield systematic control over both shape and size in the sub-10 nm domain. Narrowly dispersed particles are achieved by the ligand exchange-induced stepwise growth of (8–13 nm) particles that exhibit pronounced cuboidal morphology.

2. Characterization

2.1. High-Resolution Transmission Electron Microscopy

Analysis on a JEOL JEM-3011 high-resolution transmission electron microscope (HRTEM) required preparation by droplet coating of particle solutions on carbon-coated Cu grids (Agar Scientific, 300 mesh). Electron optical parameters: $C_s = 0.6$ mm, $C_C = 1.2$ mm, electron energy spread = 1.5 eV, beam divergence semi-angle = 1 mrad). Elemental analysis was by energy dispersive X-ray spectroscopy (EDX). A PGT prism Si/Li detector and an Avalon 2000 analytical system were used.

The particle sizes were analyzed using Macnification 2.0.1 by counting the diameters of 100 particles (N) in higher magnification images, defining size intervals of 0.25 nm between $d_{\text{min}} \leq d \leq d_{\text{max}}$ and counting the number of particles falling into these intervals. Data were used to construct particle size distributions with DataGraph 3.0.

Particle morphology was analyzed using Digital Micrograph 3.6.5. The values of average $d$-spacing were obtained from Fourier transforms of high-magnification images ($\times800k$, $\times1M$, $\times1.2M$) using the expression $d = 20/D$ where $D$ is the diameter (nm) of rings obtained.

2.2. X-Ray Powder Diffraction

X-ray powder diffraction (XRPD) data were collected on a Roentgen PW3040/60 Xpert PRO powder X-ray diffractometer with a high-resolution PW3373/00 Cu LFF (unmonochromated) tube at $\lambda = 1.5404$ Å (Cu Kα). Sample preparation was by solvent evaporation from a colloidal solution deposited on the 0.5 mm deep ground area of a glass flat plate sample holder being just free of the reference plane of the sample stage (PW3071/60 Bracket) such that the sample was just free of the reference plane of the sample stage.

2.3. UV–Vis Spectroscopy

Data were acquired using a Perkin Elmer Lambda XLS spectrophotometer with a xenon source and 5 nm bandwidth.

3. Results and Discussion

3.1. Synthesis and Crystallographic Analysis

Previously, we have worked extensively on the preparation of metal NPs using PVP as an anti-agglomerant in sol–gel reductions of metal salt precursors. As a baseline set of experiments, Au NPs were prepared by reducing NaAuCl₄·2H₂O by ethylene glycol in an excess of PVP at 100 °C and pH 9–10 using a modified literature technique to give reproducible and monocrystalline NPs in the range 6.0–8.5 nm (Scheme 1 and Table 1, entries 1–7, see also Figure S1, Supporting Information). The variation of PVP:Au ratio was systematically studied though yielded little statistical effect on MPS and resulted only in a growth of standard deviation as the level of polymer was lowered. Last, the effect of reduction temperature on MPS was studied for a PVP:Au ratio of 25:1 (entries 8–9, cf. Entry 2) but was also found to have little effect beyond an improvement in standard deviation at 0 °C.

In a similar vein, the documented Na₃Cit reduction of [AuCl₄]⁻ was attempted. This proved reproducible for Na₃Cit:Au ratios in the range 25:1–3.5:1, rendering narrowly dispersed Au NPs from 15.0 ± 2.1 nm to 19.9 ± 2.1 nm that were highly polycrystalline (that is, NPs that had agglomerated readily with respect to electric bilayer formation; see Figure S6, Supporting Information). In our hands, reactions utilizing a significant excess of citrate (100:1 with respect to Au) proved highly irreproducible (Scheme 2 and Table 2). Although an MPS could be obtained by TEM (12.4 ± 1.7 nm) the NPs formed in tandem with a number of poorly defined, highly agglomerated species.

We were intrigued by the recent report that dramatic effects could be had on the mean sizes of Au NPs generated using Na₃Cit by manipulating the concentration of this reducing agent.

In order to target Au NPs with an MPS smaller than has been traditionally achieved using Na₃Cit but greater than that associated with steric capping agents, we sought to modulate

| Entry | PVP:Au ratio | MPS | SD  |
|-------|--------------|-----|-----|
| 1°    | 100:1        | 6.17 ± 1.03 | 16.7% |
| 2°    | 25:1         | 5.96 ± 1.16 | 19.4% |
| 3°    | 10:1         | 6.54 ± 1.46 | 22.3% |
| 4°    | 7:1          | 6.84 ± 1.79 | 26.2% |
| 5°    | 5:1          | 6.73 ± 1.99 | 29.6% |
| 6°    | 3.5:1        | 7.47 ± 2.28 | 30.5% |
| 7°    | 2:1          | 8.53 ± 2.51 | 29.4% |
| 8°    | 25:1         | 5.02 ± 0.89 | 17.7% |
| 9°    | 25:1         | 6.52 ± 1.39 | 21.3% |

Reduction at °100, °50, °197 °C.
citrate concentration using PVP. With previous work having established that a minimum in MPS was achieved by citrate reduction utilizing a Na₃Cit/Au ratio of 3.5,[12] we initially treated aqueous NaAuCl₄ with aqueous Na₃Cit·2H₂O (3.5–100 eq. with respect to Au, Table 3 entries 1–5) and equimolar PVP at room temperature with stirring before heating to reflux and maintaining this for 20 min before quenching in an ice bath (Scheme 3). Analysis of the resulting colloids revealed intriguing results. Entry 1 gave only aggregated species, which can be attributed to the rapid reduction of Au⁺¹ by the large excess of citrate. Such a scenario affords very high local concentrations of NP seeds, which then agglomerate before PVP-capping can occur. However, entries 2–4 reveal the ready ability to render monodisperse NPs with a MPS of 10.4–10.8 nm and an impressive standard deviation (±1.0 nm). Notably, a close analysis of the TEM data points to these NPs being highly polycrystalline in nature (Figure 1a). We attribute this to the contrast between the rapid rate at which PVP (precoated to the metal ions) can act as a steric capping agent (giving sub-10 nm nanocrystallites) and the much slower formation of an electric bilayer by trisodium citrate (which occurs post-NP synthesis and favors substantially larger agglomerates).

Overall therefore, whereas this newly developed hybrid synthesis affords a simple and reliable, one-pot route to 10 nm Au NPs, morphological control is intrinsically limited. For the systems described in entries 2–4, this manifests itself as a poorly spherical nature to the individual particles. Taken together, these observations can be rationalized in terms of the strongly reducing nature of trisodium citrate inducing rapid nucleation that is followed by agglomeration rather than an extended particle growth phase.

Entry 5 reveals the formation of NPs with significantly different morphologies to those noted above. Accordingly, the deployment of a 3.5:3.5:1 Na₃Cit:PVP:Au ratio gave particles that displayed a consistent aspect ratio of 1.8:1 (Figure 1c). This is clearly evidenced by the observation of a size distribution whose bimodal structure highlights the difference between the lengths and diameters of 100 particles (Figure 1e). The implication of data noted for entries 1–5 in Table 3 is that as the level of Na₃Cit is lowered the reaction ceases to operate under the kinetic control of this component. Instead, lower levels of citrate favor increased growth/agglomeration phases relative to those seen in entries 2–4. Whereas the observation of elongated nanoparticles might initially suggest the selective binding of Na₃Cit and PVP to differently indexed planes of the emerging Au nanocrystals, the persistence of a 1.8:1 aspect ratio instead suggests that particle geometry results from the agglomeration of two constituent seed particles.

This mechanism can be rationalized in terms of there being insufficient PVP present to completely cap all of the emerging seeds and so to fully preclude agglomeration. In order to test this theory, a 1:1:1 Na₃Cit:PVP:Au ratio was investigated. The expected dominance of PVP over the synthesis when using only 1 eq. Na₃Cit was clearly evidenced by the return to spherical aspect ratios of 10.35 ± 0.66 nm NPs by TEM (Figure 1d). Notably, by ensuring that PVP was not in excess the growth phase was limited such that a remarkably low standard deviation could be seen (entry 6). This last point is borne out by the final hybrid Na₃Cit/PVP reactions studied (entries 7–8) in which inequivalent levels of either component were used. Hence, the use of either an excess of Na₃Cit (over-nucleation followed by agglomeration) or of PVP (limited nucleation followed by an extended growth phase) resulted in inferior size distributions. Ensuring that the minimum quantity of PVP was used also meant that the resulting particles did not suffer from the same degree of contamination that has previously inhibited the use of other PVP-capped particles in electrical and electrochemical applications. However, it should be noted that the polymeric nature of PVP and the chelating effect of its many oxygen centres will still inhibit its post-synthetic removal.

Having developed synthetic work to the point where Au NPs could be fabricated not only in the 5–9 and 15–20 nm regions but also in the intermediate 10 nm regime by a new hybrid polymer-salt methodology, we next sought to focus on controlling

Table 2. Summary of Na₃Cit-reduced systems.

| Entry | Na₃Cit:Au ratio | MPS       | SD      |
|-------|----------------|-----------|---------|
| 1     | 100:1          | 12.42 ± 1.65⁴ | 13.2%   |
| 2     | 25:1           | 15.02 ± 2.09  | 13.9%   |
| 3     | 7:1            | 17.93 ± 2.84  | 15.8%   |
| 4     | 3.5:1          | 19.92 ± 2.09  | 10.5%   |

⁴Agglomerated species noted also.

Table 3. Au NPs prepared by a hybrid PVP/Na₃Cit reduction method.

| Entry | Na₃Cit:PVP:Au | MPS       | SD      |
|-------|----------------|-----------|---------|
| 1     | 100:100:1      | Aggregated | –       |
| 2     | 25:25:1        | 10.84 ± 1.02  | 9.4%    |
| 3     | 10:10:1        | 10.59 ± 0.85  | 8.0%    |
| 4     | 7:7:1          | 10.38 ± 1.01  | 9.7%    |
| 5     | 3.5:3.5:1      | 24.95±1.69  | 6.8%    |
| 6     | 3.5:3.5:1      | 13.93 ± 1.68  | 12.1%   |
| 7     | 1:1:1          | 10.35 ± 0.66  | 6.4%    |
| 8     | 3.5:7:1        | 15.57 ± 4.11  | 26.3%   |

Scheme 2. Preparation of Au NPs by citrate reduction (n = 3.5–100).

Scheme 3. Preparation of 10 nm Au NPs using a hybrid PVP/Na₃Cit reduction route (n = 1–100).
Figure 1. Monodisperse Au NPs prepared by a PVP/Na₃Cit method at a) ×800k magnification reveal a highly polycrystalline nature (Table 3, Entry 3), while b,c) the use of a citrate:PVP:Au ratio of 3.5:3.5:1 resulted in the agglomeration of pairs of NPs (Table 3, Entry 5; shown at ×150k and ×800k magnification) and d) spherical NPs (×300k) were obtained under PVP control using a 1:1:1 reagent ratio (Table 3, Entry 6); e) the formation of anisotropic NPs (image b) with two distinct diametric measurements (orange = diameters, purple = lengths) as reflected by their bimodal size distribution ($n = 100$ for both histograms).
NP size while decreasing particle anisotropy by using straight-chain, molecular capping agents.[17]

It is widely accepted that to introduce biocompatibility and functionalizability to a NP a gold shell is an excellent candidate.[18] However, whereas the coating of XFe₂O₄ (X = Fe, Mn, Co) with Au has been claimed based on the reduction of gold salts on premade seeds using oleic acid (OA), oleylamine (OAm) with 1,2-hexadecanediol reductant,[15] we noted that the alternative use of much cheaper 1,2-tetradecanediol (TDD) failed to give core@shell XFe₂O₄@Au but instead directly yielded monometallic Au NPs. We subsequently refined this method in the absence of XFe₂O₄ (Scheme 4, Table 4).

The use of a 1:4 OA:OAm ratio was selected based on recent literature[15] and reduction conditions of 30, 90, and 240 min at reflux were tested for a variety of OA:Au ratios. HRTEM analysis revealed that the resulting NPs fall in same size regime as Au NPs produced by the use of PVP (Table 1). However, in contrast to the results obtained using polymer, the new route allowed the generation of NPs with significantly improved standard deviations. This was borne of their highly spherical nature (Figure 2a), which we attribute to the uniformity with which long-chain molecular capping agents may coat the surface of the growing particles. Extending the reduction phase had little clear effect; it led to a slight increase in MPS (with substantial agglomeration at 240 min) and generally to a small decrease in standard deviation. However, the trend towards smaller MPS at increased OA:Au ratios was clear (Figure 2b).

Only a limited number of reports exist detailing the controlled growth of Au NPs by ligand exchange.[19] Notably, previous reports of the growth of Au NPs with MPSs comparable to those obtained using TDD reductant have been based on the two-stage synthesis of 7.2 ± 1.2 nm Au NPs[11] by the replacement of triphenylphosphine capping agents by 1-pentadecylamine (PDA). In our hands, this technique was extended to reveal the synthesis of highly novel Au NPs with cuboidal geometry. In contrast to the systems studied thus far, we now sought to study shape effects in the stepwise growth of Au NPs starting from Au₅₅(PPh₃)₁₂Cl₆,[20] with the introduction

$$\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6 \xrightarrow{\text{PDA}} \text{Au NPs}$$

Table 4. Au NPs prepared by a TDD reduction method in the presence of straight-chain, molecular capping agents.

| Entry | OA:OAm:Au ratio | MPS   | SD  |
|-------|-----------------|-------|-----|
| 1     | 3.5:14:1        | 6.33 ± 1.52 | 23.3% |
| 2     | 3.5:14:1        | 7.20 ± 1.17 | 16.3% |
| 3     | 3.5:14:1        | Aggregated | –   |
| 4     | 5:20:1          | 4.29 ± 0.72 | 16.78% |
| 5     | 5:20:1          | 6.18 ± 0.88 | 14.2% |
| 6     | 5:20:1          | Aggregated | –   |
| 7     | 7.5:30:1        | 4.03 ± 0.52 | 12.9% |
| 8     | 7.5:30:1        | 5.13 ± 0.84 | 16.4% |
| 9     | 7.5:30:1        | Aggregated | –   |
| 10    | 10:40:1         | 3.82 ± 0.56 | 14.5% |
| 11    | 10:40:1         | 5.01 ± 0.57 | 11.4% |
| 12    | 10:40:1         | Aggregated | –   |

Figure 2. a) Narrowly dispersed, highly isotropic Au NPs prepared by a TDD reduction method imaged at ×300k (Table 4, Entry 7), and b) the trend towards smaller MPS at increased OA:Au ratios (Table 4, Entries 2, 5, 8, 11) (n = 100 for all size distributions).

Scheme 5. Growth of cuboidal Au NPs by the replacement of PPh₃ ligands by those of PDA over 12 d.
Growth of gold nanoparticles was initiated by the exchange between triphenylphosphine ligands capping the gold surface and pentadecylamine ligands in solution. a,b) The ligand exchange-induced growth of Au NPs over 12 d affords highly monodisperse particles (11.52 ± 0.81 nm). c) After 6 d, pairs of conjoined NPs are observable generating a twinning plane (highlighted), with d) subsequent growth at the Au(111) plane giving distinct cuboidal material with an excellent monodispersity (n = 100, SD = 7.0%).

The remarkable appearance of the NPs after 12 d of ligand exchange (Figure 3a) provides indicators for their method of formation. As noted for the synthesis of Au NPs, using a 3.5:3.5:1 Na3Cit:PVP:Au ratio, the incomplete capping of growing NPs by PVP may allow their agglomeration to give dimers with characteristic aspect ratios. We consider that in the present case, of exchange between PPh3 and PDA, a similar process occurs and results in the formation of two-particle aggregates with a clearly visible twinning plane (Figure 3c).[21] As this plane is close-packed,[22] it follows that subsequent growth will occur parallel to it,[23] providing that such growth is not inhibited by preferential PDA coordination. The characteristic shape of PDA resulting in the synthesis of narrowly dispersed 4.32 ± 0.87, 6.55 ± 0.91, and 9.42 ± 1.11 nm particles after 3, 6, and 9 d, respectively (Scheme 5, Figure 3). In line with previous observations, the replacement of PPh3 by PDA improved particle size distribution from 19.3% in Au55(PPh3)12Cl6 to 11.8% after 9 d as ligand exchange is accompanied by significant NP growth with essential retention of spherical aspect ratio. However, prolonging of the exchange-induced growth phase results in significant alterations after 12 d. Accordingly, size distribution dropped dramatically to render the final NPs 11.52 ± 0.81 nm (SD = 7.0%) and the individual particles adopted a cuboidal geometry.

The only exception to this is the problematic sample prepared using a 100-fold excess of Na3Cit, where the presence of very large agglomerates ensured a low concentration of small NPs and so prevented the observation of a clear \( \lambda_{\text{max}} \). On the face of it, these observations are contradictory, whereas the more defined maximum certainly suggests improved dispersity (as seen in Table 2), the decreased \( \lambda_{\text{max}} \) is consistent with smaller NPs. Two possible explanations present themselves. First, HRTEM reveals that the NPs observed after Au(III) reduction by Na3Cit are highly polycrystalline with the spectroscopic observations potentially being influenced by the optoelectronic properties of the smaller and agglomerated nanocrystallites that result from the use of a more aggressive reducing agent (cf. Na3Cit vs EG). Second, the electronegativity associated with the O-centers in the citrate capping agent may withdraw electron density from the metal and so lower the Fermi level.

This rationalization of \( \lambda_{\text{max}} \) being at ca. 528 nm for NPs prepared by the new hybrid Na3Cit/PVP route concurs with the view that reaction occurs under the kinetic control of citrate reduction and the observation (by HRTEM) that polycrystalline NPs dominate (see the previous section). The only exception to this trend lies in the spectroscopic data obtained for particles prepared using a 3.5:3.5:1 Na3Cit:PVP:Au ratio (Table 3, Entry 5, and also Figure 4), where two \( \lambda_{\text{max}} \) values (of 530 and 581 nm) manifest themselves, in line with literature expectation[25] based on the observation of anisotropic NPs with a reproducible aspect ratio of 1.8:1.

As summarized in Table 4, attempts to enhance morphological control by deploying TDD to reduce Au(III) in the presence of a 1:4 OA:OAm revealed a general trend towards smaller NPs as...
the OA:Au ratio was increased. At any given OA:Au ratio reduction times of 30, 90, and 240 min were tested, with the latter giving only large agglomerates (Table 4, Entries 3, 6, 9, and 12). Correspondingly, only very broad, low-intensity $\lambda_{\text{max}}$ values of ca. 540–550 nm were seen spectroscopically (see Table S8, Supporting Information). Hence, for example, representative data for the 7.5:30:1 OA:OAm:Au series of reactions are plotted in Figure 4 and reveal a broad, weak peak at 545 nm. Samples prepared over 90 min, all revealed weak maxima, which moved to lower wavelength in line with a decrease in MPS (Table 4, Entries 2, 5, 8, 11, and Table S8, Supporting Information). For the series of reactions illustrated in Figure 4 the 5.13 ± 0.84 nm obtained after 90 min revealed a $\lambda_{\text{max}}$ value of 523 nm.

The four 30 min reductions afforded the smallest NPs obtained using TDD, again with a trend towards smaller MPS as the OA:Au ratio was raised (Table 4, Entries 1, 4, 7, 10). These samples yielded the lowest $\lambda_{\text{max}}$ values of any produced by this route, with Figure 4 revealing a maximum at 515 nm attributable to 4.03 ± 0.52 nm colloids.

Last, the controlled growth of Au NPs was monitored, with data reinforcing the view that NPs grow from spectroscopically transparent Au $55(P\text{Ph}_3)^{12}\text{Cl}_6$ seeds to give clear $\lambda_{\text{max}}$ values of 530, 536, and 544 nm after 3, 6, and 9 d (MPS = 4.32 ± 0.87 nm and 6.55 ± 0.91 and 9.42 ± 1.11 nm, respectively). However, the continued development of both mean size and particle morphology resulted in depletion of the plasmonic resonance after longer growth periods.

4. Conclusions

We have shown that, whereas PVP and trisodium-citrate-modulated Au NP syntheses give particles in the ranges 6.0–8.5 nm and 15.0–19.9 nm, respectively, the development of a hybrid method has allowed convenient preparation of monodisperse NPs in the intermediate size regime. Rationalization of the competing mechanisms by which electrostatic bilayer and steric capping agent coverage of NP surfaces develops has also enabled us to understand the distinct particle aspect ratio and spectroscopic profile seen for NPs formed when equimolar Na$_3$Cit and PVP were used in slight excess with respect to Au. The precise nature of any interactions between Na$_3$Cit and PVP in solution has not yet been investigated, and this represents a focus of ongoing work, whereby we are seeking to more fully understand the competing effects of electrostatic and steric capping. Such a study will also benefit from an in-depth analysis of the ligand kinetics involved, monitored by in situ UV–vis spectroscopic techniques. In seeking to develop control not only over NP size but also shape, the deployment of straight-chain, molecular capping agents proved highly profitable, whereas ligand exchange successfully allowed the controlled evolution of spherical NPs into cuboidal ones.

5. Experimental Section

Synthesis of PVP-Capped Au NPs: NaAuCl$_4$·2H$_2$O (0.010 g, 0.025 mmol) was dissolved in water (MiliQ, 5 mL). A solution of PVP (average $M_w = 10\,000$, amount varied according to Table 1) in ethylene glycol (90 mL) was obtained by stirring at 80 °C for 2 h. The latter solution was added to the former one and the resulting mixture was stirred for 15 min before being cooled to 0 °C. The pH was adjusted to ca. 9 by adding NaOH (1 M in MiliQ water, 5 mL). The reaction was stirred at 0,
100, or 197 °C for 90 min to give a crude NP dispersion, an aliquot of which was purified by extraction using excess acetone (1:10) over not more than 240 min. After sedimentation of the particles, the supernatant was decanted and the remaining suspension centrifuged. Upon removal of the solvent layer, the precipitate was re-suspended in ethanol.

**Synthesis of Citrate-Capped Au NPs**: Sodium citrate tribasic dihydrate (amount varied, see Supporting Information) was dissolved in water (MiliQ, 95 mL) and the mixture was heated to reflux. To that solution, one of NaAuCl₄·2H₂O (0.010 g, 0.025 mmol in 5 mL MiliQ water) was added. The resulting mixture was stirred for 20 min after which the reaction was quenched by removing the heat source. Samples were used without further purification.

**Hybrid PVP/Trisodium Citrate Synthesis of Au NPs**: Trisodium citrate basic tribasic dihydrate (variable amount, see Supporting Information) was added. The resulting mixture was stirred for 20 min after which the reaction was quenched by removing the heat source. Samples were used without further purification.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author. It includes synthetic, electron microscopic and EDX data.

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