Control of shape and surface crystallography of gold nanocrystals for electrochemical applications

Ying Chen\textsuperscript{a,b,1,*}, Ashwin Anthony Fernandes\textsuperscript{a,2}, Andreas Erbe\textsuperscript{a}

\textsuperscript{a}Department of Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf, Germany

\textsuperscript{b}Center for Electrochemical Sciences, Ruhr-Universität Bochum, Universitätstr. 150, 44780 Bochum, Germany

Abstract

Colloidal gold particles can be easily produced by the reaction between HAuCl\textsubscript{4} and N,N-dimethylformamide (DMF) without the presence of any capping agent. Depending on the amount of H\textsubscript{2}O in the reaction mixture (0 to 98 vol\%), the shape of the produced Au particles resemble a rhombic dodecahedron (3–5 vol\% H\textsubscript{2}O), a horned rhombic dodecahedron (i.e. a rhombic dodecahedron with horn-like features over every second corner, 5–7 vol\% H\textsubscript{2}O), a wire or a thin plate (>20 vol\% H\textsubscript{2}O). The crystallographic orientation of the particle was studied by X-ray diffraction, surface crystallography was determined by a study of the Au oxidation. Particles in which \{110\} surfaces dominate can be prepared, as well as particles where the lowest energy \{111\} surface dominates. The function of water in the reaction is discussed.

*Corresponding author; Phone: +49 89 289 12542, Fax: +49 89 289 12536

Email addresses: ying.chen@tum.de, chenying135@gmail.com (Ying Chen), a.erbe@mpie.de, aerbe@arcor.de (Andreas Erbe)

\textsuperscript{1}Current address: Physik-Department E19, Technische Universität München, James-Franck-Str. 1, 85748 Garching

\textsuperscript{2}Current address: Institute of Process Engineering, Swiss Federal Institute of Technology (ETH), Sonneggstrasse 3, 8092 ETH Zürich, Switzerland

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\textsuperscript{1}Current address: Institute of Process Engineering, Swiss Federal Institute of Technology (ETH), Sonneggstrasse 3, 8092 ETH Zürich, Switzerland
The method used here presents a versatile way for the preparation of gold particles with many different shapes with minor alteration of the procedure. 

**Keywords:** shape control, gold colloids, water concentration, electrochemistry

1. Introduction

Controlling the shape during the synthesis of colloidal metal particles, here referred to as micro-/nano-particles (MNPs), has been a major research focus in the last decade [1–5]. This interest stems mainly from the resulting exposure of different surface facets [1, 6, 7]. Because of the difference in atomic arrangement, different crystallographic facets show differences not only in the physical properties, but also in their chemical activities, e.g. in catalytic reactions or electrocatalytic reactions [1, 2, 5, 8, 9]. The investigation of the shape control of MNPs proved to be fruitful. However, most of the synthetic methods are based on practical experience and include complicated procedures which, in turn, can not easily repeated by other labs [1, 2, 5, 7].

Moreover, it still remains challenging to control the shape of MNPs by simple variation of a single parameter in the synthesis procedure, because typically only MNPs with one or two specific shapes can be obtained through one synthetic method. Metal MNPS are mostly synthesized by reduction of metal salts as metal precursor by a reducing agent in the presence of organic molecules, so-called 'capping agents', to control the shape of particles [7, 8, 10–12]. The exposed surfaces of crystals during growth can be controlled through adsorption-desorption processes of the organic capping agents. The capping agents can also act as reducing agent simultaneously [8, 10, 12].
Alternatively, the etching by certain substances in a specific crystal direction leads to shape control [13]. By the nature of most of the synthetic methods, the surface of the obtained MNPs are coated with organic substances [2, 8]. By washing, the surface coverage with adsorbed materials can be reduced, but complete removal is impossible due to the strong interaction between the metal and the adsorbed molecules [9, 14]. The absorbed organic species on the surface in turn affect the surface reactivity, and present a serious obstacle in the application of MNPs, such as in catalysts and sensors sensing process [8, 15, 16]. The complete removal of the stabilizing agent without inducing significant surface reorganization, melting or oxidation can be achieved, but is difficult and may introduce other impurities [8, 9, 14–16].

The ideal synthesis method for Au MNPs therefore enables a shape control without the need of a capping agent. But, as set forth, the shape and size control becomes extremely difficult in this case [8]. Recently, the synthesis was reported of gold nanoparticles with the shape of rhombic dodecahedron by reducing chloroaucric acid with N,N-dimethylformamide (DMF) without the presence of any capping agent [17]. Due to the low temperature during the reaction, the slow growth kinetics led to the formation of crystallographic facet of \{110\} with much higher surface energy compared with the other two low index surfaces, the \{111\} and \{100\} surfaces. Subsequently, a higher reaction temperature was used in the same system to obtain singly twinned squashed dodecahedron particles, which are terminated by \{110\} planes and separated by one \{111\} twinning plane [18]. In both cases, the reaction between H\text{AuCl}_4 and DMF can be formulated as one step reduction of AuCl$_4^-$.
directly to Au⁰ [10, 19, 20]:

\[ 3\text{HCON(CH}_3\text{)}_2 + 2\text{AuCl}_4^- + 3\text{H}_2\text{O} \rightarrow 2\text{Au}^0 + 3(\text{CH}_3)_2\text{NCOOH} + 6\text{H}^+ + 8\text{Cl}^- . \quad (1) \]

Alternatively, the reaction can proceed through two steps if AuCl₃ is used as the gold precursor [20]:

\[ \text{HCON(CH}_3\text{)}_2 + \text{Au}^{3+} + \text{H}_2\text{O} \rightarrow \text{Au}^+ + (\text{CH}_3)_2\text{NCOOH} + 2\text{H}^+ \quad (2) \]

\[ 3\text{HCON(CH}_3\text{)}_2 + 2\text{Au}^{3+} + 3\text{H}_2\text{O} \rightarrow 2\text{Au}^0 + 3(\text{CH}_3)_2\text{NCOOH} + 6\text{H}^+ \quad (3) \]

The successful synthesis of nanocrystals with \{110\} is exciting due to the higher surface energy of the \{110\} surface, resulting in higher catalytic activity. Further, the use of DMF provides a capping agent free method for the shape controlled synthesis. However, only one shape was obtained by this method. In present study, the effect is investigated of the volume fraction of \text{H}_2\text{O} in the reaction mixture on the resulting shape of the obtained MNPs. The electrochemical reactivity towards the gold oxidation is subsequently used to characterise the surface termination.

2. Experimental

Chloroauric acid (HAuCl₄ · \text{H}_2\text{O}) was purchased from Alfa Aesar, and the other reagents were purchased from VWR International. All reagents were used as received without further purification.

For the synthesis of gold MNPs, 0.417 mL 48 mM HAuCl₄ solution in DMF was added to a mixture of DMF and water. The volume fraction of \text{H}_2\text{O} was varied from 0 to 98 volume-% while keeping the total reaction volume as
25 mL. (All the water concentration in the text is given as volume percent of the sum of the volumes of the individual components.) The reactant mixture was thoroughly mixed in a glass reaction vessel and heated in an oven to 95±5 °C for ≈15 h. The reaction vessel was subsequently taken out and left to cool to room temperature. The resultant Au MNPs were purified by centrifugation (3000 rpm for 3 minutes) and washing with either ethanol or H₂O to remove excess DMF.

A field emission scanning electron microscope (FE-SEM, LEO 1550VP, GEMINI) was used for observing the morphology of the particles. X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8 X-ray diffractometer with a Cu-Kα source. For peak identification in the diffraction patterns, the Diffrac Plus database JCPDS, File No. 04-0784 was used. The samples for SEM and XRD were prepared by dipping a drop of the gold MNP suspension onto a clean Si wafer (for SEM) or glass (for XRD) and drying under ambient condition.

For electrochemical measurements, a glassy carbon electrode (diameter of 3 mm surrounded by Teflon) was used as supporting electrode and carefully polished and washed before each experiment. The gold MNP suspension was dripped onto the surface of the glassy carbon electrode and dried with N₂ stream. Cyclic voltammograms (CVs) were recorded with an Ivium compactstat (Ivium, The Netherlands) at room temperature (ca. (22 ± 2)°C) in a conventional three-electrode electrochemical cell. The counter electrode was a pure gold plate and the reference electrode was an Ag/AgCl electrode (in 3 M KCl, Metrohm AG, +208 mV versus the standard hydrogen electrode (SHE)). All the potentials indicated in this article are versus SHE. All
electrolytes for the electrochemical reactions were deoxygenated by bubbling with high purity Ar for 20 min before each measurement. All the glassware was cleaned by a freshly prepared mixture of 98 % H$_2$SO$_4$ : 30% H$_2$O$_2$ = 3 : 1 (vv) (“Piranha solution”).

3. Results

No formation of gold particles was observed without addition of water to the solution. Even after addition of H$_2$O to 0.5 %, no gold particles were obtained. Only the colour of the solution changed from light yellow to transparent colourless if small amounts of water are present. A colourless solution cannot contain significant amounts of gold particles [8, 10, 12, 21].

When the volume fraction of H$_2$O reaches 1 %, a small amount of solid precipitation is observed in the solution. The amount of the solid product increases with the volume fraction of H$_2$O. Fig. 1 shows the SEM images of the obtained Au MNPs with the H$_2$O concentration between 1 and 8 %. As one can see from Fig. 1 a and b, when the concentration of H$_2$O is below 3 %, the predominant morphology exhibited by the particles is irregular jagged, along with the occasional presence of regular, highly symmetric particles. The shape of the MNPs is not uniform, but it can be divided into two categories: (a) more than 90 % of the particles are big irregular ”meatball”–like with an average diameter of 3–4 μm and (b) smaller particles (less than 10 %) showing highly symmetric shapes, with average diameters <1 μm. The portion of the small regular particles increased when the concentration of H$_2$O increased from 1 % to 2 % (see Fig. 1b). With further increasing of the H$_2$O content to 3 %, a pronounced change is observed. Most of the particles
obtained show a rhombic dodecahedral shape with an average diameter of about 700 – 1000 nm, as seen in Fig. 1c. The shape of the particles remains the same when H$_2$O concentration is between 3 and 5%. Gold nanoparticles in the shape of rhombic dodecahedra have been reported previously, including a discussion of their structure [17]. The particle diameter obtained in this work is slightly larger compared with ref [17]. A possible difference in the reaction temperature could be the reason for this difference.

Upon further increase in the water concentration, rhombic dodecahedral particles with tipped edges become the predominant morphology of the prod-
uct, as shown in Fig. 1d. This transition is noticed when the water concentration is higher than 5 %, but below 8 %. As the tips on the particle’s corners resemble “horns”, the particles will be termed “horned rhombic dodecahedra”. The portion of the horned rhombic dodecahedron particles is maximum when the H₂O concentration is \( \approx 6 \) %. An enlarged view of the horned rhombic dodecahedron indicates that horns grow on the edge where three surfaces cross, as indicated in Fig. 1d inset. The surface on the top of the horn, according the face-centred cubic (fcc) lattice, should be a \{111\} surface. A detailed analysis will be shown below.

In the composition region of H₂O content between 5 and 7 %, the \{110\} facet is still dominant, though the \{111\} facet starts to appear. The solvent/reagent mixture therefore first of all ensures nucleation of metal particles, while presumably adsorption of different species to different surfaces regulates the crystal growth. In particular, also the adsorption of water must play a role to explain the different shapes observed in the low water composition region.

In subsequent experiments, the concentration of H₂O was further increased. Fig. 2 shows the particles obtained when the concentration of H₂O is increased to 8 or 10 %. The diameter of the particles decreases, and the edges of the rhombic dodecahedral particles become blurred, more like for spherical particles. With 8 % of H₂O, some horns can still be seen, as shown in Fig. 2a, though less than at lower water content. The number of horns on the surface is decreasing to almost zero when the H₂O concentration is 10 % (Fig. 2b). At the same time, as shown in Fig. 2b inset, some big plate-shaped and tetrahedrally shaped (with one truncated vertex) crystals start to ap-
Figure 2: SEM image of the gold MNPs obtained with 8 % (a, b, c) and 10 % (d, e, f) of H$_2$O concentration. (b, c) show an enlarged view of particles with horns, which shorten with increasing water content. (e, f) show the enlarged view of particles in the shapes of spheres and plates. The scale bars are 2 µm for (a, d), and 500 nm for (b, c, e, f).

pear in the product. The plate and tetrahedron for gold are typically enclosed solely by \{111\} surfaces [5, 7, 8]. The portion of \{111\} surface on the obtained crystals increases significantly with the increase in the concentration of H$_2$O. Starting from 5 % of H$_2$O content, the \{110\} facet of the obtained crystals ceased to exist and a near spherical shape was obtained when H$_2$O
between 8 and 10%. A strong shift in the morphology is observed when $\text{H}_2\text{O}$

Figure 3: FE-SEM image of the gold MNPs obtained with $\text{H}_2\text{O}$ concentration of (a) 16 vol.%, (b) 20%, (c) 30%, (d) 50%, and (e, f) 98%. The inset in (a) shows the typical shapes obtained, i.e., rod, truncated tetrahedron and octahedron. All of these crystals show the $\{111\}$ surface as the exposed surface. The scale bars are 2$\mu$m for a–f, and 500 nm for inset in (a).

concentration was further increased as not only the shape but also the size of the obtained MNPs changes qualitatively. In Fig. 3a, showing particles

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obtained from a reaction mixture with 16 % H₂O concentration, most of the obtained particles have the shape of a truncated tetrahedron, octahedron, rod or plate. The tetrahedron and octahedron have a size less than 500 nm. The rods have a diameter about 200 nm and length of 2-3 µm. The plate diameters are about 2-3 µm. The tip of the rods shows a penta-twinned structure (Fig. 3a top inset). The penta-twinned structured nanocrystals are one common product in gold nanorod or nanowire syntheses, and have been discussed in detail elsewhere [5, 7, 8, 12, 22, 23]. To avoid repetition, here we are not discussing this in detail. It should be pointed out though that the predominant crystallographic orientation of the surface of the nanowires is also {111}. The plates show a hexagonal or triangular shape, which is also the most common product in the nanoplate syntheses [12, 22, 24, 25]. Due to the smaller size, the colour of the solution after the reaction is brick red, and the dispersions of gold particles are stable over several hours. When the H₂O concentration is increased to 20 %, the portion of plates in the product increases, as shown in Fig. 3b. The plates have a hexagonal shape and diameters about 2 – 3 µm. Meanwhile, there are more wires of length >10 µm present in the product.

The portion of the nanoplates and nanorods in the product increases further when the concentration of H₂O increases to 30 %, as indicated in Fig. 3c. In this composition range, the nanoplates and nanowires are the main product. There is only a small fraction of spherically or octahedrally shaped particles. When 50 % of H₂O is present in the reaction mixture, the main product are nanoplates. Nanowires are almost absent (Fig. 3d). Fig. 3 e and f show SEM images of the product obtained at extremely high
water concentrations (98 %), (0.417 mL of 48 mM HAuCl$_4$ DMF solution mixed with 24.5 mL H$_2$O). Here, thin plates or film-like plates become the main product. The thin plates form a network of interconnected particles. These networks cannot be dispersed in solution easily, even by sonication, the networks settle at the bottom of the container. The surface of the plates should be dominated by the \{111\} surface.

For a full characterisation of the particles, crystallographic information about the particles is needed. One effective way is transmission electron microscopy (TEM) [7], however, due to the big size of some of the produced particles ($\approx \mu$m), conventional TEM is not applicable here. Instead, X-ray diffraction (XRD) can be used to assess the overall crystallinity and phase purity of the MNPs with different shapes. Fig. 4 shows the XRD patterns of the MNPs obtained at different H$_2$O concentration. For a better comparison, all peaks are normalised to the peak located at scattering angle $2\theta = 38^\circ$, the strongest peak for polycrystalline gold. The XRD pattern indicates that all of the MNPs are the fcc gold (JCPDS, file number 04-0784). The comparison of the different diffraction peak intensities yields features which are intrinsically correlated to the shapes of the MNPs [26, 27].

Assuming a random distribution of the particles, information about the relative preference of the different growth directions in the crystals can be extracted. The relative intensity of the peaks changed significantly for different shaped MNPs, especially for the peak at $2\theta = 64.5^\circ$, which is corresponding to \{110\} planes. When the concentration of the H$_2$O is below 2.5 %, the relative intensity of \{110\} reflection is about 1.7, which is much higher than the value of 0.32 for polycrystalline gold. At this H$_2$O concentration, the
most particles show a meatball-like shape, where many tiny crystallographic surfaces are present. This may be the reason that this kind of crystal shows a strong diffraction peak at $2\theta = 64.5^\circ$. The intensity of the $\{110\}$ peak changes to 3.0 with the increase of $\text{H}_2\text{O}$ content to 3 %. This means that the faces of the rhombic dodecahedral shaped $\text{fcc}$ crystals, primarily composed of $\{110\}$ planes, tend to preferentially orient parallel to the supporting substrates, thus giving a significant diffraction intensity in (220) direction. With further increasing of $\text{H}_2\text{O}$ concentration, tips have appeared on the corners of the rhombic dodecahedra (Fig. 1d). At the same time, the intensity of the peaks for $\{110\}$ planes decreased significantly to $\approx 0.46$. This is a clear indication that the appearing tips at the corners of the rhombic dodecahedron are enclosed by $\{111\}$ faces. The decrease in the $\{110\}$ peak and the appearance of $\{111\}$ peak is induced by a slight change in the concentration of $\text{H}_2\text{O}$. 

Figure 4: X-ray diffraction patterns of the gold MNPs synthesized with different $\text{H}_2\text{O}$ concentration.
the reaction. The intensity ratio between the (220) and the (111) diffraction peaks is further decreased to about 0.13 (even lower than the bulk value) for the MNPs obtained at H$_2$O concentration of 10%. With even higher H$_2$O concentration, the peak corresponding to {110} surface at 2$\theta$ = 64.5° is almost completely missing, showing that this direction is not dominating the termination of the crystals at higher H$_2$O concentration. Instead, the intensity of the peak for {111} direction is so strong that almost no other peaks are present at all. This again indicates that for MNPs obtained at H$_2$O concentration higher than 10%, the {111} family of planes is dominant. The dramatic change of different peak intensities, although it cannot be seen as the direct evidence of the preferential growth crystallographic orientations, it is a nice hint for this trend, typically combined with the observations of the shapes of the MNPs.

The actual surface termination in aqueous solution can be determined by testing the different particles towards their reactivity in a specific electrochemical reaction. This method is sensitive to the surface termination only. It has been proven that cyclic voltammetry (CV) is very sensitive to the surface conditions of the test electrode and can be used to characterise not only macroscopic electrodes, but also electrodes made from nanoparticles [16, 28, 28]. The sensitivity of voltammetric behaviour of gold single crystal electrodes is first measured to check the sensitivity of the method in 0.01 M H$_2$SO$_4$, as shown in Fig. 5a. The electrochemical behaviour of {111} and {110} oriented Au electrodes are rather different in the region where the gold oxide monolayer forms (1.2–1.6 V). The oxidation of gold on different surfaces shows quite different oxidation potentials. The main oxidation po-
Figure 5: Cyclic voltammograms in 0.01 M H$_2$SO$_4$ of (a) single crystal gold electrode and (b) gold MNPs on glassy carbon electrode obtained with different H$_2$O concentration. (c) Enlarged CV curves for the positive scan in the region of 1.2 – 1.6 V for Au MNPs. Scan rate: 20 mV/s.
potential for a \{111\} surface is about 1.52 V, accompanied by a small shoulder peak at 1.3 V. For the \{110\} surface, the main oxidation peak is located at 1.32 V, 200 mV lower than that of \{111\}, followed by a broad shoulder peak between 1.38 and 1.47 V. Fig. 5b shows the CVs in 0.01 M H$_2$SO$_4$ of Au MNPs synthesised with different H$_2$O concentration. Fig. 5c shows the enlarged view in the gold oxide formation region, 1.2 – 1.6 V. The CVs of particles obtained at low H$_2$O concentration (below 3 %, shapes are mainly meatball-like or rhombic dodecahedral) shows one sharp oxidation current peak at 1.28 V and a broad shoulder peak around 1.33–1.37 V. Comparison with the CVs of \{111\} and \{110\} single crystal gold electrodes shows this behaviour to be identical with the behaviour of gold \{110\} surface. It is accordance with the results obtained from XRD. When the H$_2$O concentration is increased to 6 %, where the horned rhombic dodecahedral particles are the main product, the CV shows similar current peaks as for the gold \{110\} surface, but the peaks, especially the shoulder peak, are positively shifted about 50 mV. This peak shift to a higher potential may indicate the transition of \{110\} to \{111\} surface, or the presence of many facet boundaries. With even higher H$_2$O concentration, the CVs of the particles show only a main peak at 1.47 V, typical for the nanoplates obtained at 98 % of H$_2$O. The surface-sensitive electrochemical oxidation proves for the transition from \{110\} terminated particles obtained at low H$_2$O content to \{111\} terminated particles at higher H$_2$O content in the reaction.
4. Discussion

According to both mechanisms (reactions 1-3), the reaction cannot proceed without the presence of H$_2$O. The presence of water is inevitable under the experimental conditions used here, because the gold precursor is HAuCl$_4$·2H$_2$O, which contains two molecules of crystal H$_2$O, and DMF is used as received without further dehydration. Under these conditions, the content of H$_2$O should be sufficient for the reaction to proceed (compare reactions 1-3). However, no formation of gold particles was observed for solution with a water volume fraction below 1%.

With 0.5 % water, there is, however, a colour change of the solution, indicating that a reaction took place. One explanation is reaction 2, where Au$^{3+}$ is reduced to Au$^+$, not Au$^0$. Au$^+$ solutions are typically colourless [29]. For a further reduction of the produced Au$^+$, the nucleation barrier may be too high for particle formation to occur; Au$^0$ seeds (< 1 nm) or poly(vinypyrrolidone) (PVP) were used overcome this barrier [10, 20, 30, 31]. Apparently, no nucleating agent is present here, thus no Au particles were obtained. Water may act as a cosolvent, enabling reactions 1 - 3.

A critical amount of water over the stochiometric fraction is needed for particle formation to occur. The presence of water is therefore crucial in the nucleation of gold MNPs. The different preferable surface terminations at different solvent compositions may be related to the different stabilities of the respective surface in different environment. More likely, however, adsorption of DMF, H$_2$O, or one of the reaction products on the different particle surfaces plays a crucial role in determining the shape. A candidate species which could determine growth is the carbamic acid or carbamate forming
as reaction product, as shown in reactions 1 – 3. In aqueous environment, the reaction product N,N-dimethylcarbamic acid, dissociates. Pure DMF is a much weaker base than H$_2$O. It is therefore likely that an increase in the content of H$_2$O facilitates dissociation, leading to various species in the solution with distinct adsorption properties on the different Au surfaces. Alternatively, water adsorption on the different surfaces may also be responsible for the observations. Addition of N,N-dimethylcarbamic acid or the respective salt may therefore be useful to control the shape of the particles more precisely than presented here, if this mechanism is indeed shape-determining.

A second effect of water is the destabilisation of the intermediate Au$^+$ species formed as a product of reaction 2. In aqueous environments, Au$^+$ tends to disproportionate to Au$^0$ and Au$^{3+}$ [29]. The formed Au$^0$ can combine to form particles.

Third, there is also an effect of the water contents on the kinetics of reactions 1 – 3. As water is a reactant in all three reactions, and therefore, gold reduction should become faster with an overall increase of the water concentration. Faster reaction, in turn, should imply faster growth of crystals, and a consequent faster disappearance of the less stable (faster growing) surfaces, the \{110\} surface in this case. As a result of fast reaction, the final shape of the Au MNPs turned to be plate-shape which is almost solely enclosed by \{111\} surface.

5. Conclusions

The same reaction, the reduction of AuCl$_4^-$ with DMF in the presence of H$_2$O, yields gold MNPs of quite different shapes and sizes depending on
the amount of H$_2$O in the reaction. This method is extremely easy. No capping agent is necessary to prepare and control the shapes of the obtained MNPs. The absence of capping agent in the nanoparticle preparation have an advantage that the surfaces of the particles are cleaner than when surfactants are present in the solutions. While low water content in the reaction mixture leads to particles predominantly with a \{110\} surface, the more stable \{111\} surface is preferably formed at higher water contents, as has been shown in the CVs using Au-oxidation as indicator reaction. The obtained shapes versus water contents are summarised in Fig. 6.

![Figure 6: Obtained shapes of Au MNPs for DMF reduction in dependence of the water volume fraction in the solution.](image)

The produced clean nanoparticles are expected to have substantially different electrocatalytic and sensing properties than the particles prepared in other syntheses. This synthesis method opens up the possibility to obtain particles with substantially different shapes from one synthesis method, import in reactivity studies. The way for the shape control in metal nanoparticle preparations could also be extended to other systems.
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References


Highlights

- Au particle shape control by adjusting composition of DMF/H$_2$O mixtures
- at low H$_2$O content $\{110\}$ surfaces dominate the rhombic dodecahedron shaped MNPs
- at high H$_2$O content, $\{111\}$ surfaces dominate the plate shaped MNPs
- cyclic voltammetry proved the crystallographic orientations of different shaped MNPs
Graphical abstract