21 October 2025

NaBH4-mediated syntheses of colloidal gold nanocatalysts in water: are additives really needed?

Hilary Kouawa Fokam[1], Aleksandra Smolska[1], Jonathan Quinson[1,2]

1. Aarhus University
2. Universidade da Coruña

verall, the results stress the benefits of surfactant-free approaches to develop gold-based nanomaterials and provide guidelines to optimize their synthesis towards more sustainable nanotechnologies.

Keywords

NaBH₄-mediated syntheses of colloidal gold nanocatalysts in water: are additives really needed?

Hilary Kouawa Fokam,[a] Aleksandra Smolska,[a] Jonathan Quinson[a,b]*

a) Biological and Chemical Engineering Department, Aarhus University, 8200 Aarhus, Denmark
b) CICA-Centro Interdisciplinar de Química e Bioloxía, Facultade de Ciencias, Universidade da Coruña, Campus de Elviña, A Coruña, Spain

* corresponding author: jquinson@bce.au.dk, j.quinson@udc.es

Abstract

Gold (Au) nanoparticles (NPs) are relevant for multiple applications in electronics, sensing, bio-medicine, optics, catalysis and many more. As a consequence, a range of colloidal syntheses have been reported where a gold precursor is reduced to metallic Au NPs. In numerous protocols, stabilizers such as surfactants are added to ensure colloidal stability and/or achieve size control. The actual *need* for such added chemicals, often derived from fossil fuels, is rarely questioned. Here, we investigate the effect(s), pros and cons of using common additives such as sodium citrate (NaCt), polyvinlypyrrolidone (PVP) or sodium dodecylsulfate (SDS), in the fast (seconds) room temperature synthesis of Au NPs obtained otherwise by using only water and NaBH₄ in its *surfactant-free* version. The effect of the NaBH₄/Au molar ratio, the Additive/Au molar ratio and the concentration of HAuCl₄ used as precursor are jointly investigated in parametric study over 130 samples. The influence of the order of addition of the chemicals is also discussed. It is found that there is no benefit to use the additives considering size control, stability but also catalysis. A fine control over the NP size in the range 3-10 nm is easily achieved without additives by controlling the NaBH₄/Au molar ratio. A benefit of PVP is to lead to NPs smaller than 3 nm even at relatively high concentration of HAuCl₄ up to 3-4 mM. An advantage of the additive-free approach is not only to develop simpler and more sustainable syntheses of colloidal NPs stale over time, but also to lead in most cases to more catalysts as or even more active compared to NPs prepared with additives. This is exemplified with the 4-nitrophenol reduction for a model reaction for water treatment and the ethanol electrocatalytic oxidation (EOR) as a model reaction for energy conversion. Finally, the surfactant-free approach is shown to be easily scalable to 1 L of solution, e.g. by a factor x500 compared to the parametric study performed. Overall, the results stress the benefits of surfactant-free approaches to develop gold-based nanomaterials and provide guidelines to optimize their synthesis towards more sustainable nanotechnologies.

Introduction

Due to their unique size, morphology and composition dependent properties, nanomaterials offer a unique range of opportunities for various applications in electronics, medicine, sensing, catalysis, water/air treatment and many more.[1-5] An optimized use of a nanomaterial requires its careful synthesis. A range of synthetic methods have been reported and are largely exploited to prepare various nanoparticles (NPs).[6,7] In particular, colloidal NPs prepared in the liquid phase by reduction of a metal precursor are used worldwide and have already benefited various areas of fundamental and applied research.[7-9] In most cases, in addition to a metal precursor, a solvent and a reducing agent, a range of *stabilizers / capping agents / ligands / surfactants / additives / shape directing agents / protective agents* are claimed to be required to achieve successful syntheses of NPs, control NP size, stability and/or crystal structure.[1,10-14] While those additives can indeed help obtaining specific NP shapes with unique properties, or even bring specific functionalities to the nanomaterials,[12] they can also be detrimental to applications such as in medicine where 'clean' NPs might be required and/or catalysis since the additives can potentially block active sites.[14,15] Furthermore, those additives are often derived from fossil fuels,[16] thus not optimal to holistically address sustainability, environmental matters and *green* chemistry, which would require that the NP syntheses themselves are more sustainable,[17,18] regardless of the application.

Nanomaterials syntheses remain heavily based on trials-and-errors.[19] Despite the increasing understanding of several syntheses towards a more rational design of various NPs,[11,20] it remains challenging to anticipate which chemicals are required and how to select the right amount of each of them for a successful synthesis.[7] In other words, it remains unclear which chemicals are *truly* and *minimally* needed to achieve a given outcome. As a consequence, it is also relatively poorly studied what the effect of the preparation methods and the choice of a stabilizer can have on the resulting properties of the NPs. There is a lack of 'control' experiments, or 'blank' samples where a successful synthesis is achieved in the first place without the additives or stabilizers. If they were more widely available, such *surfactant-free* model systems could guide the rational design of more advanced materials, as discussed and anticipated elsewhere.[14,21]

In particular, Au NPs are a widely studied class of materials due to their biocompatibility, plasmonic properties and catalytic properties.[22,23] Various colloidal syntheses of Au NPs have been reported, where the most iconic are probably the Borowskaja-Turkevich-Frens method,[11,24,25] performed in water close to the boiling point using citrate as reducing and stabilizing agent, or the Brust-Schiffrin methods using $NaBH_4$ as reducing agent and thiols molecules as stabilizers.[26,27] However, simpler and potentially more sustainable syntheses, e.g. requiring safer and fewer chemicals,[6,17] could be greatly beneficial to facilitate the widespread use of NPs by non-experts in NP preparation, make the most of NP properties, and/or contribute to understanding the actual need and/or roles of various chemicals selected rather empirically to date. In this respect, so-called *surfactant-free* syntheses are appealing. *Surfactant-free* syntheses can be defined as syntheses where no other chemical than the metal precursor has a molar mass higher than 100 g mol^{-1}, as detailed elsewhere.[14] In other words, only relatively small size molecules or charged species play the role of stabilizers.

In the quest to understand and optimize colloidal syntheses, we showed that various surfactant-free colloidal syntheses of metal NPs can be developed.[21,28-30] Tremiliosi-Filho and co-workers showed that no additives were needed when water, glycerol and a base were used for the room temperature synthesis of sub-10 nm Au NPs.[31] We showed that glycerol can be substituted with ethylene glycol[32] or ethanol[29] to develop more sustainable syntheses in low(er) boiling point solvents. We also established that adding various molecules commonly used in several colloidal syntheses did not lead to any significant advantage over the surfactant-free version of the ethanol-mediated synthesis.[33]

2/23

Actually, using additives resulted in lower stability and/or larger NPs in most cases. Although those surfactant-free approaches might not lead to the most monodispersed samples or the most fine control over the NP structure, they lead to production methods requiring few chemicals with the potential to be easily implemented by non-experts,[34,35] promising for real-life production and implementation.[14,28,29] Furthermore, due to their relatively *free* surface, those surfactant-free approaches tend to lead to nano-catalysts with higher catalytic activity than the state-of-the-art.[28,29,34]

We here investigate and clarify the actual need for additives in $NaBH_4$-mediated room temperature syntheses of Au NPs in water. It is worth stressing that this method presents the advantage to only require water as a green solvent,[36] which makes it ideal for applications in medicine or catalysis given that the resulting NPs are free (or as free as currently possible) of potential organic residues. $NaBH_4$ is a very common reducing agent for Au nanomaterial synthesis, in part due to its ability to reduce gold precursor at room temperature in seconds.[37] Astruc and co-workers showed that when $NaBH_4$ is used as reducing agent, there is no need for any other chemicals to obtain stable colloidal NPs.[34] A similar approach was used by Iqbal et al.,[38] as well as Larm et al. to prepare Au_xAg_{1-x} NPs,[39,40] see details in **Table S1** in **supporting information** (**SI**). Nevertheless, a much wider range of syntheses and body of literature including $NaBH_4$-mediated syntheses of Au NPs still prefer and report the use of citrate (NaCt),[11,41,42] polyvinylpyrrolidone (PVP)[43,44] or sodium dodecylsulfate (SDS).[45,46] Other reported chemicals, among many options, could be tanic acid,[47] ascorbic acid,[47] tritonX[48] or CTAB.[49]

Here, we first aim to investigate the actual need and potential benefits for various additives (none, NaCt, PVP, SDS) in $NaBH_4$-mediated syntheses of Au NPs in water for various $HAuCl_4$ precursor concentrations (0.1, 0.2, 0.5 mM), various $NaBH_4$/Au molar ratios (5, 8, 10) and various additives/Au molar ratios (0, 5, 10, 15) when it comes to size control and stability of the NPs. Those values and chemicals were selected as representative of values commonly used in various protocols in the literature, to cover a broad parameter space, and because they are commonly investigated across various reports, as detailed in **SI** in the experimental section. A first goal is to question the actual need of such chemicals and identify a strategy to develop more sustainable syntheses. Secondly, we aim to clarify the potential pros and cons of surfactant-free Au NPs for catalysis. Third, we show the potential scalability of the most promising method. The results challenge the quasi-dogmatic view and the statement almost systematically found in the literature that additives are *needed* to develop successful syntheses of colloidal Au NPs.[14,50,51] The pros and cons of surfactant-free syntheses, i.e. syntheses requiring as little as possible of only as few chemicals as possible, are illustrated for both size control and stability of colloidal Au NPs and for their catalytic properties for the 4-nitrophenol (4-NP) reduction and the ethanol oxidation reaction (EOR).

Scope

While control over NP properties across a broad size range is ultimately a general goal,[51,52] here, to facilitate the discussion below, it is considered that a synthesis is optimal if it (i) leads to small size NPs (more likely to be stable and relevant for catalysis since smaller Au NPs tend to be more active[53]); (ii) requires few chemicals (ultimately leading to a process simpler, cheaper and less sensitive to contamination[54]); (iii) requires low amount of chemicals (ultimately cheaper, more likely to scale up, in line with the principles of green and sustainable chemistry[6]); (iv) can be performed at high $HAuCl_4$ concentration (because then less volume of solvent is required to produce a given amount of Au NPs).

A wide range of additives can be used for $NaBH_4$-mediated syntheses. Here, NaCt was selected for its wide use as stabilizing agent in Au NP syntheses.[11,42] NaCt can also play the role of reducing agent,[37] but the synthesis is poorly controlled at room-temperature if $NaBH_4$ is not used. PVP was selected for its wide use in Au NP synthesis and NPs in general.[43] PVP, a non-ionic polymer, can also play the role

of reducing agent,[37] but the synthesis is poorly controlled at room temperature if NaBH$_4$ is not used. SDS was selected as a common ionic surfactant with very minimal reducing properties.[46,55] Other common additives such as tannic acid, ascorbic acid where excluded due to their relatively strong reducing properties.[47] CTAB is another widely used chemical in Au nanomaterial syntheses.[49,56] However, this chemicals is relatively harmful and would ideally be avoided to develop syntheses method compatible with the principles of *green* and *sustainable* chemistry in nanoscience.[6,17] For the same reasons, water is here preferred as solvent, although NaBH$_4$-mediated syntheses were reported in alternative solvents such as methanol.[57] It is not excluded that alternative solvents and chemicals could be relevant to study beyond the examples proposed below in this first report for an even deeper understanding of Au NPs and the development of (even more) sustainable syntheses.

Materials and Methods

Extensive details on the Au NP syntheses, their characterization, procedures followed and metrics retrieved for the catalytic assessment are provided in **SI**. In particular, UV-vis measurements and the metrics retrieved together with their signification are detailed in **Table S2**. The general synthesis methods follow an approach reported by Astruc and co-workers with mofifications.[34] The samples considered for this study are reported in **Table S3**.

Results and discussion

1. General synthesis concept

Adding $NaBH_4$ to an aqueous solution of $HAuCl_4$ leads in few seconds to the formation of orange-red colloidal dispersions, characterized by a surface plasmon resonance (spr) with an absorption maximum in UV-vis characterization around 510 nm, which corresponds to spherical NPs ca. 5 nm in diameter. The reaction proceeds without or with additives. An illustration of the synthesis process, together with illustrative UV-vis and STEM data are reported in **Figure 1**. Illustrative XRD data confirming the formation of fcc Au NPs is reported in **Figure S1**.
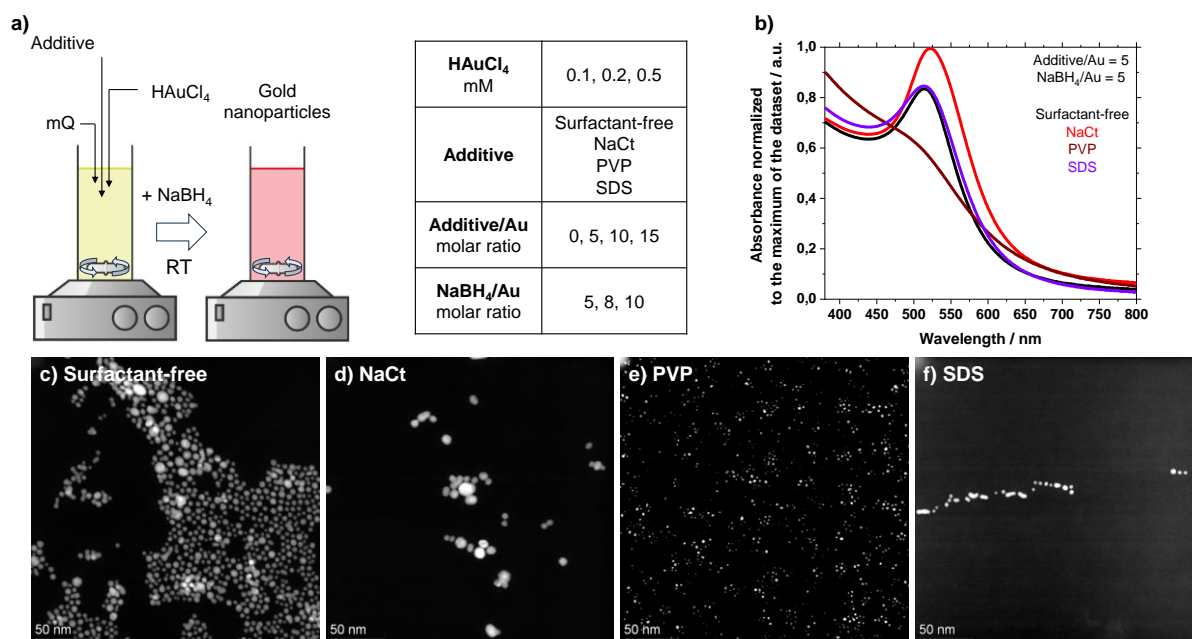

Figure 1. (a) Scheme of the room temperature $NaBH_4$-mediated synthesis of Au NPs. Created with Chemix (2025). Retrieved from https://chemix.org and adapted. RT stands for room temperature (b) Illustrative UV-vis and (c-f) STEM micrographs of Au NPs obtained (c) without additives, (d) with NaCt, (e) PVP, (f) SDS, as indicated, for a $HAuCl_4$ concentration of 0.5 mM, a $NaBH_4$/Au molar ratio of 5 and an Additive/Au molar ratio of 5. The more blurry background in (f) comes from contamination from SDS that interacts with the high-energy beam of the microscope.

2. Parametric study

First, the effects of using or not various additives at similar Additive/Au molar ratio, for various $HAuCl_4$ concentrations and $NaBH_4$/Au molar ratios were investigated. When no additives are used, an increasing $NaBH_4$/Au molar ratio leads to larger NPs. This is in particular very clear at higher $HAuCl_4$ concentrations, as illustrated in **Figure 2a**, with a shift of the λ_{spr} towards larger wavelengths that correlates well with a size increase evaluated by STEM. The size control achieved is finer than in previous reports,[34,39] because a finer $NaBH_4$/Au molar ratio was screened and here the influence of the $HAuCl_4$ concentration is also considered.

For 0.1 mM $HAuCl_4$, the size for a $NaBH_4$/Au molar ratio of 5, 8, 10 is 4.7 ± 0.9 nm, 4.4 ± 0.8 nm, 4.8 ± 0.9, respectively for λ_{spr} values of 510, 510, 510 nm, respectively, and A_{spr}/A_{450} values of 1.23, 1.21, 1.24, respectively. For 0.2 mM $HAuCl_4$, the size for a $NaBH_4$/Au molar ratio of 5, 8, 10 is 4.0 ± 0.8 nm, 4.4 ± 1.3 nm, 4.8 ± 0.9 nm, respectively for λ_{spr} values of 508, 514, 512 nm, respectively, and A_{spr}/A_{450} values of 1.17, 1.27, 1.26, respectively. For 0.25 mM $HAuCl_4$, the size for a $NaBH_4$/Au molar ratio of 5,

8, 10 is 5.5 ± 2.1 nm, 4.4 ± 1.2 nm, 5.2 ± 1.3 nm, respectively for λ_{spr} values of 514, 510, 514 nm, respectively, and A_{spr}/A_{450} values of 1.26, 1.27, 1.29, respectively. For 0.50 mM $HAuCl_4$, the size for a $NaBH_4$/Au molar ratio of 5, 8, 10 is 4.1 ± 1.2 nm, 6.5 ± 1.3 nm, 10.0 ± 3.5 nm, respectively for λ_{spr} values of 515, 515, 520 nm, respectively, and A_{spr}/A_{450} values of 1.31, 1.43, 1.61, respectively.

To date, all studies performed relative to the surfactant-free $NaBH_4$-mediated synthesis of Au NPs were performed at fixed concentration of $HAuCl_4$, see **Table S3**. It was therefore not possible to establish exactly which parameter was key to control: the $NaBH_4$ concentration or the $NaBH_4$/Au molar ratio. By performing experiments with a same concentration of $NaBH_4$ (but different concentrations of $HAuCl_4$), different sizes are obtained which stresses that the $NaBH_4$/Au molar ratio is a better descriptor in the first place when it comes to size control. For instance using 0.10, 0.20, 0.25 and 0.50 mM $HAuCl_4$ for 1 mM $NaBH_4$ ($NaBH_4$/Au molar ratios of 10, 5, 4 and 2, respectively) leads to NPs with sizes 4.8 ± 0.9, 4.0 ± 0.8 and 3.8 ± 0.7 nm for the first three experiments and in the last case to unstable NPs more than 50 nm in size. Using 0.20 or 0.25 mM and 2.00 mM $NaBH_4$ ($NaBH_4$/Au molar ratios of 10 and 8, respectively) leads to NPs of sizes 4.8 ± 0.9 nm and 4.4 ± 1.2 nm, respectively. Using 0.50, 0.25 and 2.50 mM $NaBH_4$ ($NaBH_4$/Au molar ratios of 5 and 10, respectively) leads to NPs of sizes 4.1 ± 1.2 nm (4.0 ± 0.8 nm on a repeat) and 5.2 ± 1.3 nm, respectively. There is therefore of a stronger correlation between NP size and the $NaBH_4$/Au molar ratio than for the $HAuCl_4$ concentration or $NaBH_4$ concentration, and the NP size tends to increase when the $NaBH_4$/Au molar ratio increases above a value of ca. 4.

3. Effects of additives

The trend that higher λ_{spr} values, related to larger NPs as detailed in **Figure S2**, are obtained when the $NaBH_4$/Au molar ratios increase is also observed in presence of various additives (NaCt, PVP, SDS) at different ratios as detailed in **Figures S3**. This trend is in line with previous reports, where typically a fixed concentration of additive was used and/or a support such as Al_2O_3. For instance, using 0.6 mM $HAuCl_4$, a PVP/Au molar ratio of 1.5 and $NaBH_4$/Au molar ratio of 6.7, 8.3, 16.7, 18.3, leads to sizes of 1.7, 3.4, 5.7 and 8.2 nm.[44] The larger NPs obtained can be attributed to presence of more reducing agents leading to a more pronounced growth of the NPs.[34]

Using different additives leads to different size control, as illustrated in **Figure 2b** with the case of a $NaBH_4$/Au molar ratio of 5 and an Additive/Au molar ratio of 0 (surfactant-free) or 5 for NaCt, PVP and SDS, and different $HAuCl_4$ concentrations, as indicated. The UV-vis spectra for other $NaBH_4$/Au molar ratios and Additive/Au molar ratio are provided in **Figure S4**. The trend is that the use of NaCt leads to dispersions characterized by higher λ_{spr} values indicative of larger NPs, compared to the surfactant-free approach. PVP leads to very small NPs with almost no spr feature, compared to the surfactant-free approach. The use of SDS does not lead to any benefit compared to the surfactant-free approach. Interestingly, the use of PVP leads to stable and small size (< 5 nm) NPs across a wide experimental range. Due to their different chemical structure and functional groups, it is expected that the additives play different roles, given for instance that NaCt, as well as PVP, can play the role of reducing agents.[37] The molecules interact differently with the Au NP surface, leading to different stabilization. From the results obtained, the most efficient additive to limit the growth of the Au NPs is PVP. NaCt has a stronger effect on the stabilization of the NPs and SDS does not bring benefits compared to a surfactant-free NPs.

For a given Additive, there is trend to observe larger NPs as the amount of additive increases. This is for instance illustrated in **Figure 2c** with the example of NaCt and a $NaBH_4$/Au molar ratio of 5. Those results also illustrate the negative effect of higher concentrations of additives leading to unstable colloids, especially at higher $HAuCl_4$ concentrations, as further illustrated in **Figure S5**. This effect is

not or less observed in the surfactant-free approach. At too high concentrations of additives, additives-additives interaction might also lead to the formation of larger NP aggregates which can account for the lower colloidal stability under those conditions. In particular, the use of NaCt leads to unstable colloids characterized by overall low absorption in UV-vis measurements, see **Figure 2c**. The same tends to occur with SDS, although the effect is relatively less pronounced.
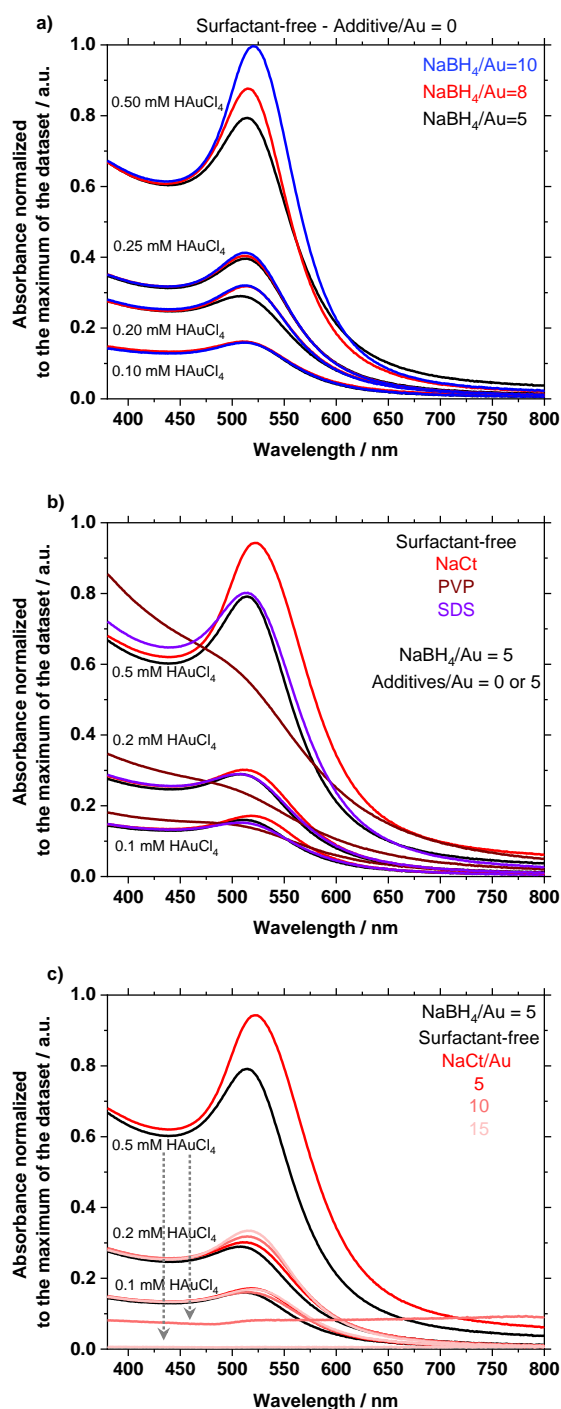

Figure 2. UV-vis spectra illustrating the effect of various variables in the synthesis of Au NPs using a room temperature NaBH$_4$-mediated approach. (a) Effect of HAuCl$_4$ concentration and NaBH$_4$/Au molar ratio for a surfactant-free synthesis. (b) Effect of using different additives, as indicated. (c) Effect of using different amounts of additives with the example of NaCt. All spectra were normalized to the

maximum of the overall dataset (a-c). Overall, as the concentration of $HAuCl_4$ increases (as indicated) the overall absorption increases. Related STEM data and analysis are given in **Figure S7**.

4. *Direct* versus *inverse* methods

It has been shown for various colloidal syntheses and for Au NPs in particular, that the order of addition of the chemicals can affect the outcome of the synthesis. For instance, in the typical Borowskaja-Turkevich-Frens method,[7,11,58] adding the $HAuCl_4$ last (often referred to as *inverse* or *reverse* conditions, as opposed to the *direct* conditions where the NaCt is added last) leads to narrower size distributions. A similar observation was made for the ethanol-mediated synthesis in alkaline conditions where the outcome of the synthesis also depends on the concentration of the stock solution of $HAuCl_4$.[29] In a nutshell, a finer size control is obtained in this last case when the gold is in its acid form, more likely to get reduced. This can be obtained by adding a concentrated solution of $HAuCl_4$ or otherwise neutral or alkaline conditions so that 'locally' the gold is in its acid form.

Here, we did not see a strong effect of the order of addition of the chemicals in the $NaBH_4$-mediated surfactant-free synthesis of Au NPs. We also assessed if the use of additives had a possible impact on the direct or inverse approach for 0.5 mM $HAuCl_4$, a $NaBH_4$/Au molar ratio of 5 and an Additive/Au molar ratio of 5. Those conditions were selected following the 'optimal' criteria defined above. The results indicate no or little effect of the order of additions of the chemicals for those conditions and especially not for the surfactant-free version, see UV-vis data in **Figures S6** and STEM data and related analysis in **Figure S8**. The little dependence on the direct or inverse method is here attributed to the strong reducing properties of $NaBH_4$ that leads to reduction in seconds.

5. Reproducibility

Reproducibility is a general challenge in the field of nanotechnology since most NP syntheses are sensitive to parameters sometimes hard to control such as light environment,[59] grade of chemicals[60] and many other 'impurities'.[61,62] The use of additives from different suppliers and/or with different grades can also account for the lack of reproducibility.[54] In the present case, the main source of irreproducibility is coming from the fact that the solution of $NaBH_4$ needs to be prepared fresh and therefore slightly different concentration of stock solution might be used across a same study.

In order to best assess reproducibility, we reproduced the conditions of 0.5 mM $HAuCl_4$, $NaBH_4$/Au molar ratio of 5 several times, as well as conditions of a NaCt/Au molar ratio of 5 and for a PVP/Au molar ratio of 5, see UV-vis data in **Figures S6**. The results suggest a relatively robust synthesis in the case where surfactant-free approach is developed or when PVP is used.

6. Optimization

The present study screens a relatively larger parameter space compared to most previous reports.[34,39,63] The incentive here was not to 'optimize' the synthesis. Rather, the trends reported here should be seen as guidelines for finer optimization on a case-by-case study. For instance, given that 0.5 mM $HAuCl_4$, a $NaBH_4$/Au molar ratio of 5, and no additives leads to smaller size NPs than when a NaCt/Au molar ratio of 5 is used, it can be expected that the NP size progressively increases as the NaCt/Au molar ratio increases from 0 to 5. This is indeed observed experimentally as reported in **Figure 3a** here using a NaCt/Au molar ratio of 1 was the only case leading to NPs with a lower λ_{spr} value but only a slightly smaller size compared to the surfactant-free approach, **Figure 3b**. Complementary STEM data and the related analysis is provided in **Figure S9**. This example shows how the present results can be used as a foundation for the selection of the additives and finer size control by the fine-

tuning of experimental parameters. The results also stress the little benefit of NaCt to fine tune the NP size below 6 nm.
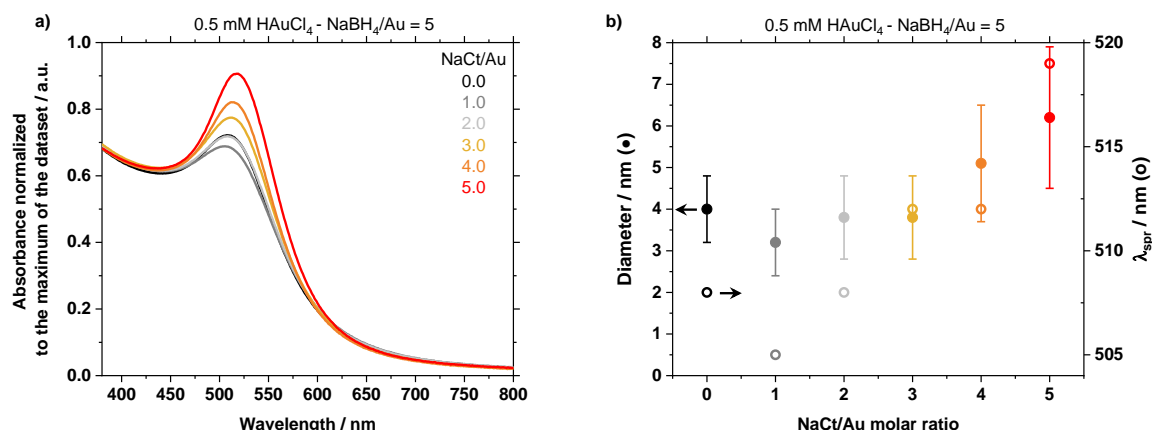

Figure 3. (a) UV-vis spectra of Au NPs prepared with various NaCt/Au molar ratio, as indicated. (b) Diameter (●, left-hand side axis) and λ_{spr} values (o, right hand-side axis) for Au NPs obtained with various NaCt/Au molar ratios, as indicated. In all cases the 0.5 mM HAuCl$_4$ and a NaBH$_4$/Au molar ratio of 5 was used. STEM micrographs and size distributions are given in **Figure S9**.

An interesting case for optimization is the use of PVP that almost regardless of the HAuCl$_4$ concentration, NaBH$_4$/Au or PVP/Au molar ratios, leads to NPs characterized by low λ_{spr} values with actually very poorly defined spr features, as illustrated in **Figure 4a**, indicative of small size NPs around 3 nm or below. This observation is encouraging to scale up the reaction. Indeed, most colloidal syntheses of Au NPs are performed in the range 0.1-0.5 mM of gold precursor.[7] Unstable colloidal NPs are typically observed at higher concentrations of HAuCl$_4$, in particular in aqueous media. The apparent robustness of the syntheses using PVP pushed us to select conditions where relatively small amounts of chemicals were used, i.e. NaBH$_4$/Au molar ratio of 5, PVP/Au molar ratio of 5, but where the HAuCl$_4$ concentration was increased to 1, 2, 3, 4 and 5 mM of HAuCl$_4$. The synthesis leads to small size NPs in all cases and stable colloids up to 3 mM HAuCl$_4$. Results are reported in **Figure 4**, the lower overall absorption decreases for higher HAuCl$_4$ concentrations of 4-5 mM, indicative of less stable NPs. The diameter of the NPs tends to increase with an increasing concentration of HAuCl$_4$, as illustrated in **Figure 4a** but the NPs remain below 3 nm in diameter, see **Figure 4b**. See also **Figure S10** for complementary STEM data and the related analysis.

Equally, since a PVP/Au molar ratio of 5 leads to very small Au NPs, and no PVP leads to also relatively small size yet larger NPs, there is probably room for fine size control. We therefore investigated PVP/Au molar ratios from 0.1-5.0 as detailed in entries 117-138 in **Table S1**. Based on UV-vis data reported in **Figure 4c**, and STEM data analysis reported in **Figure 4d**, further detailed in **Figure S11**, a relatively fine size control in the range 2-4 nm is achieved. The relatively fine size control achieved is further relevant for catalytic studies as detailed below.
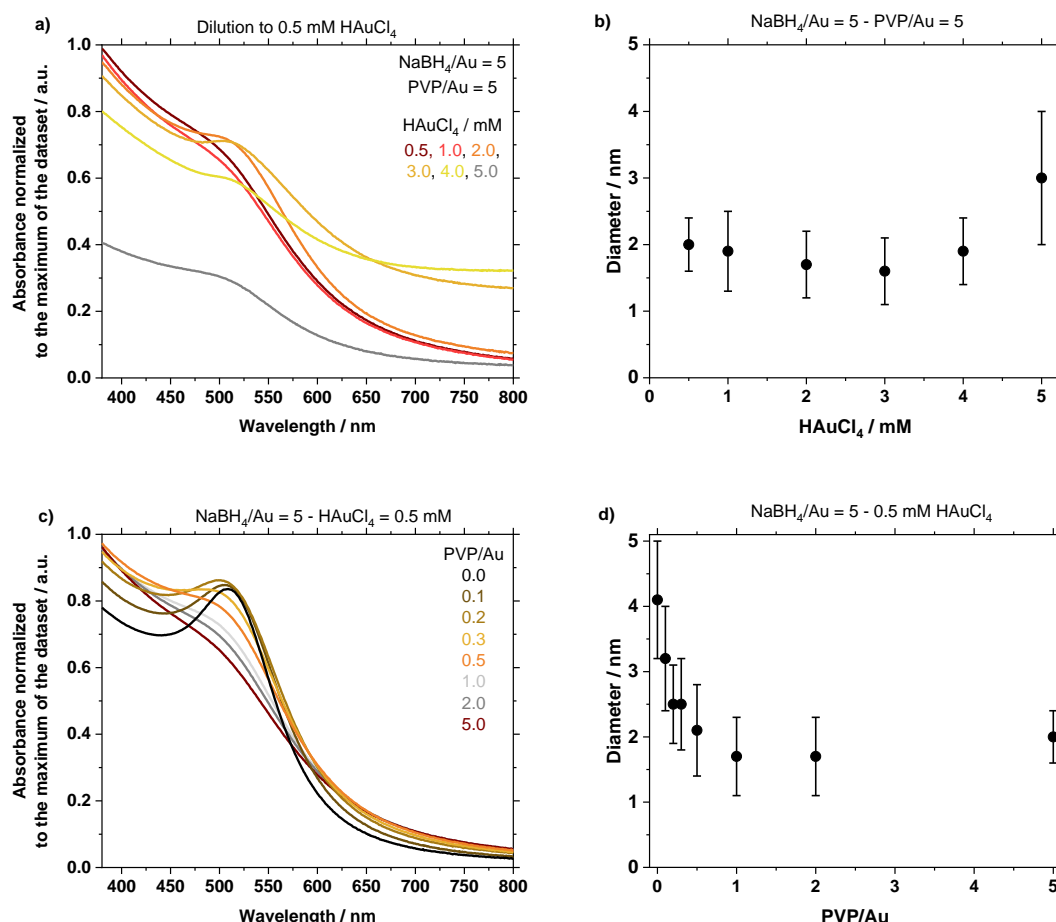
Figure 4. (a) UV-vis spectra of Au NPs prepared with various $HAuCl_4$ concentrations, as indicated, a PVP/Au molar ratio of 5 and a $NaBH_4$/Au molar ratio of 5. For measurements all samples were diluted to 0.5 mM equivalent of Au. (b) Corresponding diameter of the Au NPs, as indicated. (c) UV-vis spectra of Au NPs prepared with various PVP/Au molar ratio, as indicated, a $NaBH_4$/Au molar ratio of 5 and a $HAuCl_4$ concentration of 0.5 mM. (d) Corresponding diameter of the Au NPs. STEM micrographs and size distributions are given in **Figure S11**.

7. Stability

An important other property expected from colloidal NPs is their stability over time, i.e. their shelf life. It is often argued that stabilizers are needed and *must* be added for the sole or main purpose to guarantee the stability of the colloids. In our experience with surfactant-free syntheses and as detailed by others, this is not required.[33,64] The stability of the colloids was here evaluated by recording the UV-vis spectra of all samples after 1 month, where the samples were stored at room temperature in a drawer. The UV-vis spectra were almost identical after a month with only minor changes in the λ_{spr}, A_{450}/A_{spr}, A_{400} or A_{380}/A_{800} values, with changes typically in the range of 1-3 nm (so relatively small), 0.05 unit or less (so relatively small), ± 1-3% (so relatively small), 2-3 units (so relatively small), respectively. The stability over time was marked when NaCt and PVP were used. With no additive and with SDS there was a tendency to see slightly higher A_{spr} values as illustrated in **Figures S12-S15**.

8. Catalysis

Having established that various additives lead to different size control over the NPs, we now turn to the relevance of the process and strategies for catalysis. As model reactions, we selected the reduction of 4-NP, as well established catalytic reaction relevant to benchmark Au NPs and a model reaction for water treatment.[34,65] The use of $NaBH_4$-mediated syntheses of Au NPs is particularly relevant for this reaction that typically requires an excess of $NaBH_4$.[34,66] We also considered the ethanol oxidation reaction, as a model reaction for electro-catalysis and relevant for energy conversion.[53] To the best of our knowledge, the relevance of $NaBH_4$-mediated Au NPs for electro-catalysis has not been studied by others, see **Table S1**. Here, the goal of the comparison is to evaluate the actual need and/or benefits in using different additives in the synthesis of Au NPs. In particular, a pending question is if the use of fewer chemicals (i.e. the surfactant-free version), presents any benefits over the additive-mediated approaches that are by far more frequently reported in the literature.

Here, we voluntarily did not perform any washing of the NPs. It is therefore not excluded that *free* additives, i.e. not interacting with the Au NP surface, will be added as the Au NPs are used for catalysis. A range of approaches have been reported to remove the additives, with various degrees of success, as discussed elsewhere.[14] Attempts to remove the additives and/or clean the NP surface would require extra steps and/or immobilization on a support. The focus here is not to develop such supported materials but rather to evaluate the benefits of avoiding additives on as-prepared NPs. It must be kept in mind that the absence of additives is likely to actually facilitate any further supporting steps since the NPs are mainly stabilized by electrostatic interactions and/or small molecules.[28] Our focus here is on the strategy that develops readily active materials, without the need for extra washing or additives removal that could significantly contribute to bridge the gap between fundamental and applied research.[14,19,28]

8.1. 4-NP reduction

When following the 4-NP reduction by UV-vis catalyzed by Au NPs, as illustrated in **Figure 5a**, the use of different NPs obtained using no additives, NaCt, PVP or SDS, all lead to some degree of catalytic activity, as illustrated in **Figure 5b**, see also **Figure S16**. The most active catalysts characterized by the highest k_{app} values (see **SI** for details) and highest TOF values are obtained with the NPs prepared without additives, see **Figure 5c** and **Figure S17**. The NPs prepared using SDS and PVP lead to similar activity whereas the NPs prepared with NaCt lead to the lowest activity.

It is observed that the surfactant-free NPs are more active, which can be explained by their more accessible surface resulting from the use of $NaBH_4$ only (no additives) during the synthesis, and because $NaBH_4$ is also a chemical used here in large excess for the catalytic reduction. $NaBH_4$ was also shown to be suitable reagent to *clean* NPs surfaces and this probably explains the relatively high activity of the Au NPs prepared using SDS and PVP,[57,67] whereas the efficiency of this cleaning effect might be more moderate for Au NPs prepared with NaCt.
Another important factor to take into account is the size of the NPs. It is expected that the smallest NPs should lead to the most active catalysts.[53] This statement can be challenged in the sense that some catalytic processes show an optimal size. Too small NPs might be unstable and therefore show relatively low activity, and too large NPs show a lower surface area per mass unit, leading to lower activity. The NPs prepared using a surfactant-free approach or SDS fall into the same size range. The higher activity of the Au NPs prepared by a surfactant-free approach is then to be related to the absence of additives. The Au NPs prepared with citrate are the largest in size. The use of NaCt as an additive that is known to bind relatively strongly to the Au NP surface and the largest size of the Au NPs accounts for the overall lower activity.[68] An interesting case is the Au NPs prepared using PVP which are the smallest NPs. As such, it would be expected that their activity is significantly higher than

for the other Au NPs. However, the small size is achieved by using PVP that is known to interact rather strongly with the Au NPs surface,[29] and therefore block the active sites. The relatively high activity observed here is attributed to the small size of the Au NPs, that probably compensates for an overall low activity of the materials due to the presence of PVP, and the fact that $NaBH_4$ is likely freeing some of the related active sites. The results regarding the Au NPs prepared using PVP are therefore attributed to a balance between a small size (favoring a higher activity), the presence of an excess of $NaBH_4$ (favoring a higher activity by cleaning the NP surface), and the use of PVP (promoting a lower activity).
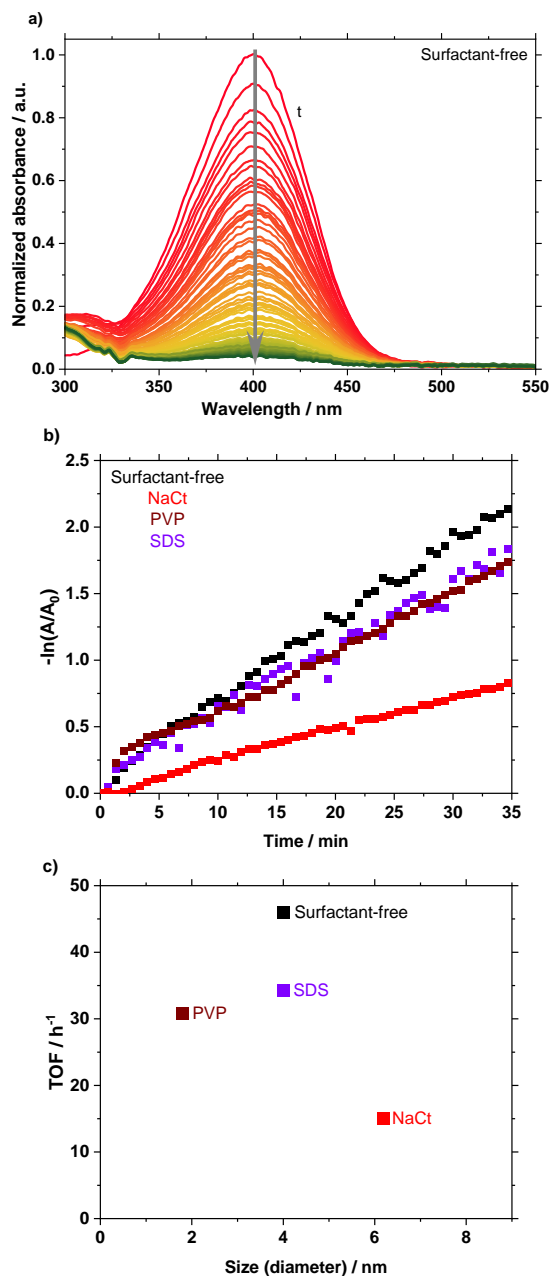

Figure 5. (a) Illustration of 4-NP reduction in presence of $NaBH_4$ catalyzed by surfactant-free Au NPs. (b) $-\ln(A/A_0)$ as a function of time used to retrieve the k_{app} values for 4-NP catalyzed by Au NPs prepared using a surfactant-free approach using NaCt, PVP or SDS, as indicated. (c) TOF values as a function of NP size. See more details in section 8 in SI, including TOF values normalized by the A_{400} values retrieved from UV-vis for the Au NP dispersions in **Figure S17**.

Overall, those results illustrate the importance of designing catalytic materials beyond active sites, and as much as possible tailor from the synthesis the features of a desirable catalyst, e.g. by developing or considering surfactant-free Au NPs. In this respect, the results show that there is no benefit to use various additives commonly employed for colloidal Au NP preparation to develop Au nanocatalysts.

The catalytic activities reached here are in the range of values reported in the literature. It must be kept in mind that the focus is here on the relative activities of the samples given that the absolute comparison with the literature can be challenging, due to various protocols employed and various ways to report the results as detailed elsewhere, i.e. challenges related to benchmarking.[60] The TOF values obtained here as in good agreement with previous preliminary results from our group using surfactant-free NaBH$_4$-mediated synthesis of Au NPs.[60] In particular, in our previous work with a stronger focus on size-effects, the TOF values obtained for Au NPs obtained by a surfactant-free NaBH$_4$-mediated synthesis were around 40 h^{-1} and 30 h^{-1} for NPs with sizes of ca. 10 and 12.5 nm respectively.[60] The here ca. 4-5 nm NPs show an expected higher TOF with a value of ca. 46 h^{-1}, which confirms the increase in activity as the NP size decreases.

8.2. Ethanol oxidation reaction (EOR)

To the best of our knowledge, the potential benefits of surfactant-free Au NPs prepared using only NaBH$_4$, water and HAuCl$_4$, have not been detailed for any other reactions than the 4-NP reduction.[34,39] A range of other heterogeneous catalytic process could benefit from this synthesis approach, and in particular electrocatalytic processes. Here, we assess the relevance of such materials to readily prepare electrocatalysts with the example of the EOR in alkaline conditions. In addition to the 4 samples already discussed above for the 4-NP reduction obtained using 0.5 mM HAuCl$_4$, NaBH$_4$/Au molar ratio of 5 and an Additive/Au molar ratio of 0 or 5, samples prepared with PVP under the same conditions but with a PVP/Au molar ratio of 0.1, 0.2, 0,3 or 0.5 were also considered.

A first important observation is that the Au NPs prepared by NaBH$_4$-mediated synthesis lead to readily active Au NPs. Several metrics retrieved from the electrocatalytic assessment are reported in **Figure 6**, such as electrochemically active surface area (ECSA) in **Figure 6a**, mass activity (MA) in **Figure 6b**, or MA after an acidic treatment (MA$_{acid}$) in **Figure 6c**. All parameters and definitions are detailed in **SI** and in particular in the **section 2.9**. A typical cyclic voltammogram for the EOR,[53] is reported in **Figure 7** and detailed in **Figure S18**. The highest MA in the forward scan, around 0.2-0.3 V$_{RHE}$ corresponds to the EOR. The highest MA on the backward scan around 0.1 V$_{RHE}$ corresponds to the electro-cleaning of the NP surface.[53] Complementary data reporting diagrams of the various metrics considered (without consideration of size effects), the same values normalized by the A$_{400}$ value retrieved from UV-vis spectroscopy, and specific activity (SA), are reported for the convenience of the reader in **Figures S19-S22** with complementary data in **Figure S23**.
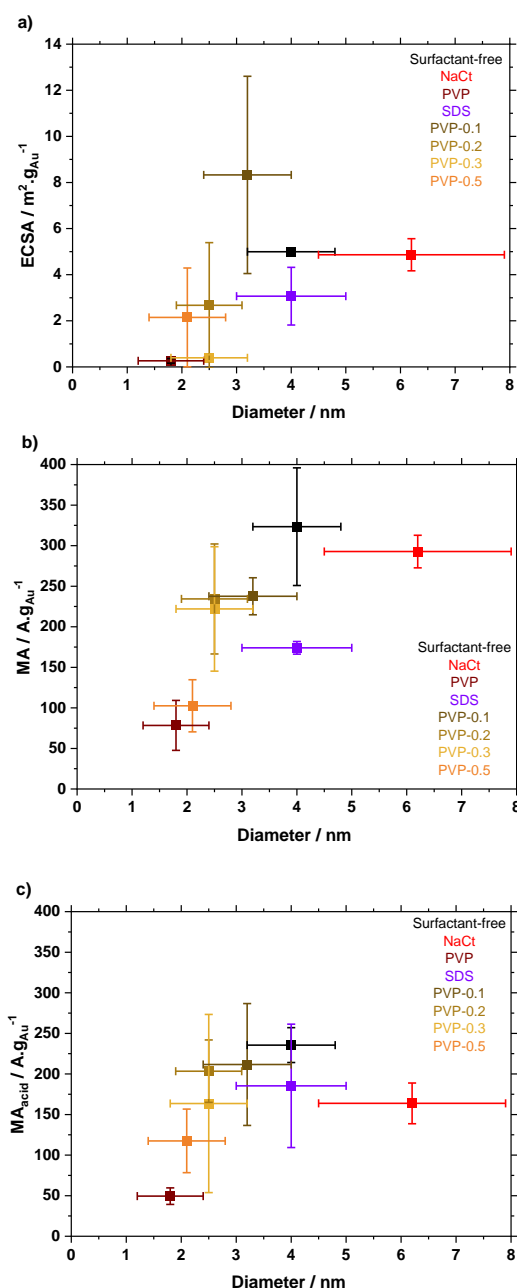
Figure 6. (a) ECSA, (b) MA and (c) MA after an acidic treatment for samples prepared without additives, with NaCt, with PVP (with various PVP/Au molar ratio of 0.1, 0.2, 0.3 or 0.5) or SDS, as indicated. Unless otherwise specified the Au NPs were prepared using 0.5 mM $HAuCl_4$, $NaBH_4$/Au molar ratio of 5 and an Additive/Au molar ratio of 5. The ECSA was evaluated in 0.5 mM H_2SO_4 and the EOR in 1 M KOH and 1 M ethanol.

Using no additive, NaCt, PVP or SDS leads to relatively active materials. The ECSA of the samples follow the trend: Surfactant-free ≈ NaCt > SDS >> PVP. The activity (MA) follows the trend: Surfactant-free > NaCt > SDS >> PVP. This trend is still observed when the Au NPs are subjected to an acid treatment (MA_{acid}), with an overall decrease of the MA values, which is attributed to a loss of Au NPs by dissolution during the oxidation-reduction process at stake during the acid step that was used to evaluate the ECSA. The MA_{acid} follows the trend: Surfactant-free > NaCt ≈ SDS >> PVP.

There is no strong relationship between the values measured and the size of the NPs, although it could be expected that the smaller NPs, owing to an expected higher ECSA, would lead to more active NPs.[53] Here, the smallest NPs obtained using PVP show the lowest ECSA and MA, which is attributed to the strong protection by PVP. It could also be that the smallest NPs are less stable under the electrochemical tests performed and therefore lead to overall lower ECSAs and MAs. In contrast, the surfactant-free version despite a relatively larger NP size leads to the most active materials with the highest ECSAs and MAs.

Given that the NPs with the smallest sizes are expected to lead to more active NPs, and given that increasing amount of PVP leads to significantly smaller NPs compared to the surfactant-free, we assessed if an optimal PVP amount to lead to more catalytically active NPs could be found. The optimal value would lead to smaller size NPs with a higher ECSA, potentially leading to higher MA, but also not enough PVP to block the active sites. Although using only a PVP/Au molar ratio of 0.1 leads to promisingly higher ECSA, **Figure 6a**, there was no benefit to use any PVP compared to the surfactant-free version of the Au NP NaBH$_4$-mediated synthesis where the MA was in the same range or lower compared to the surfactant-free Au NPs.

The surfactant-free Au NPs obtained by a surfactant-free NaBH$_4$-mediated synthesis are relatively active even over 1 hour of continuous operation in chronoamperometry (CA) as detailed in **Figure 7**. A decrease in activity is observed over time, as shown in **Figure 7b**, but the activity can be recovered as shown in cyclic voltamograms in **Figure 7a**. The decrease in activity typically observed upon CA for the EOR catalyzed by Au NPs is attributed to contamination of the Au NP surface.[69]
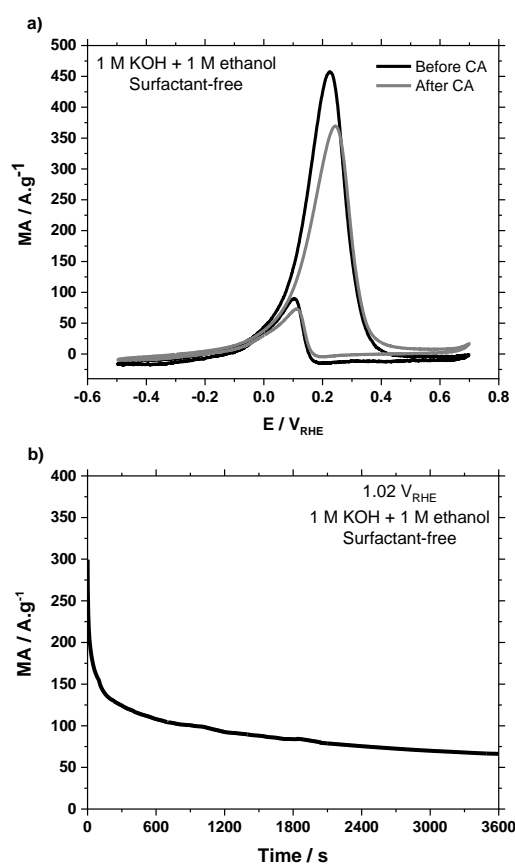

Figure 7. (a) CVs of Au NPs obtained using a surfactant-free NaBH$_4$-mediated synthesis using 0.5 mM HAuCl$_4$, a NaBH$_4$/Au molar ratio of 5 before and after CA at 1.02 V$_{RHE}$ in 1 M KOH and 1 M ethanol, recorded at a scan rate of 50 mV s^{-1}. The 10th scan is represented. (b) CA at 1.02 V$_{RHE}$ in 1 M KOH and 1 M ethanol.

It can be challenging to compare the activity of Au NPs prepared in different ways and tested following different protocols reported in the literature, as detailed elsewhere.[53] Nevertheless, the ECSAs and MAs reported here are among the highest reported for Au NMs for the EOR, as illustrated in **Table S4**. In conclusion, the surfactant-free NaBH$_4$-mediated synthesis of Au NPs led to the most active nanomaterials. This finding is promising to develop a range of syntheses based on this method and in particular the surfactant-free version of the Au NP synthesis requiring only NaBH$_4$ and HAuCl$_4$ in water.

8.3. Comparison with catalysts prepared by other surfactant-free strategies

The comparison of the catalytic activity of NPs obtained using different surfactant-free approach is almost not reported and constitutes a gap in the literature.[14] It is therefore interesting to compare the results obtained here for Au NPs prepared by a surfactant-free NaBH$_4$-mediated synthesis and those we obtained previously for Au NPs prepared using an ethanol-mediated synthesis.

For the 4-NP reduction, more active catalysts could be obtained previously by an alcohol-mediated surfactant-free synthesis, compared to the here studied surfactant-free NaBH$_4$-mediated synthesis. Although the Au NPs prepared by an ethanol-mediated synthesis show a size of around 10 nm, the NPs achieved a TOF around 50-70 h^{-1}.[60] For the EOR, the ethanol-mediated synthesis lead to Au NPs with MAs relatively high around 300 A.g$_{Au}$$^{-1}$,[53] i.e. MAs close to those obtained here with ca. 5 nm NPs with MA around 325 A.g$_{Au}$$^{-1}$. In other words, the activity increase by achieving surfactant-free Au NPs by a NaBH$_4$-mediated synthesis is not as pronounced as the significant size decrease would leave to expect (given that the NP size is divided by ca. 2 going from an ethanol-mediated to a NaBH$_4$-mediated surfactant-free synthesis). Just like the case of the 4-NP reduction, and while it is beyond the scope of this report to clarify the reason behind this observation, these results stress the importance of the synthesis approach to develop optimal catalysts. It can be expected that the smallest NPs obtained here by a NaBH$_4$-mediated synthesis are less stable which can account for the small differences in MAs.

This observation stresses the importance of the (surfactant-free) synthesis approach to develop optimal catalysts. This calls for more comparisons of surfactant-free strategies to better understand and design what makes an efficient catalyst, holistically considering all aspects of the catalyst preparation and testing, from synthesis to applications.[14,21]

9. Scalability

The results above establish the promising features of the surfactant-free NPs simply obtained using only water, HAuCl$_4$ and NaBH$_4$. Previously, a rough size control was achieved and the potential of the method to develop catalysts for the 4-NP reduction was suggested. It is here shown that the size control can be fine-tuned by tuning the NaBH$_4$/Au molar ratio in particular at relatively high HAuCl$_4$ concentrations. Moreover, it is here shown that this simple and probably overlooked surfactant-free synthesis strategy (to which an additive-mediated strategy is often preferred) is promising to lead to size-controlled Au NPs also relevant for electrocatalysis with the example of the EOR.

Those results highlight the potential of the small size NPs rapidly obtained with simple equipment for heterogeneous catalysis at large and other areas of application. A challenging aspect of most colloidal NP synthesis is the limited scalability, often related to the need to use specific equipment challenging to scale to obtain 'large batches'. The present approach has the potential to by-pass this bottleneck. In previous studies, report focused on 33 mL for 0.13 mM$_{Au}$ (ca. 0.8 mg$_{Au}$ per batch) [34] or 0.25 mM$_{Au}$

16/23

for 20 mL (ca. 1 mg$_{Au}$ per batch),[39,40] or 0.25 mM for ca. 100 mL (ca. 5 mg$_{Au}$ per batch),[38] see **Table S1**. Since our optimization was performed on small volume of solution for each sample (2 mL), and given that for further use, larger amount of NPs would be required, we investigated the possibility to scale up the synthesis to 1 L for the relatively high concentration of 0.5 mM of HAuCl$_4$. This would lead to ca. 100 mg$_{Au}$ per batch which is a more suitable quantity for various catalytic testing and further use of the NPs.
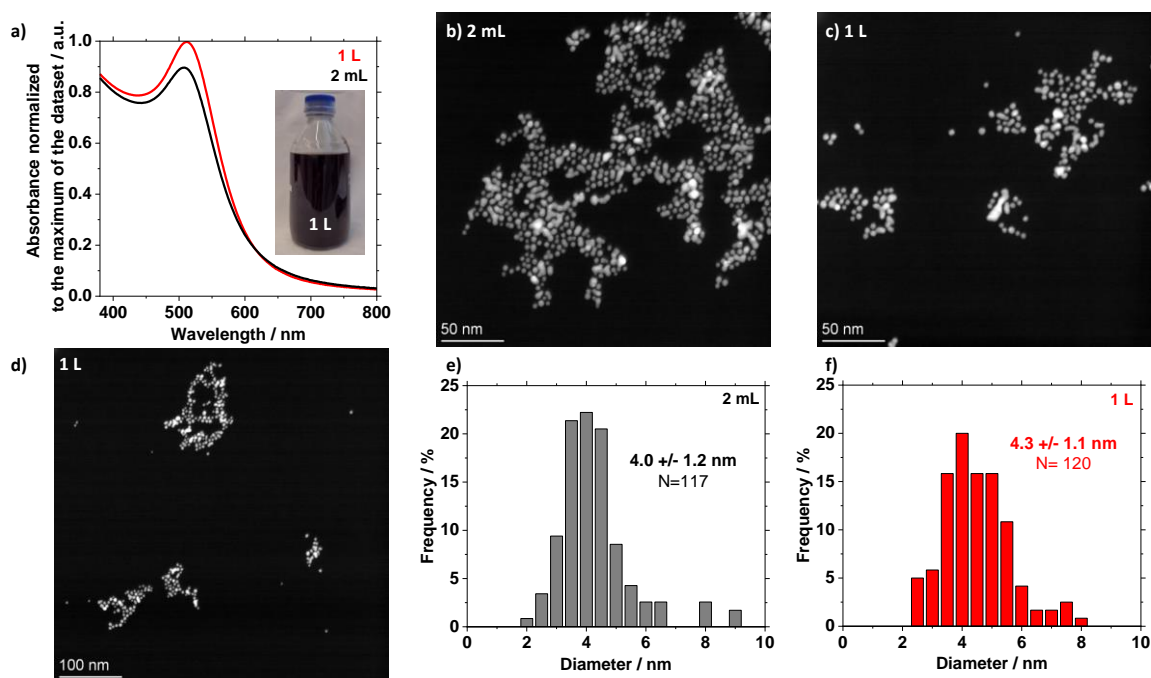

Figure 8. (a) UV-vis spectra of Au NPs prepared using a surfactant-free NaBH$_4$-mediated colloidal synthesis using 0.5 mM HAuCl$_4$ and a NaBH$_4$/Au molar ratio of 5, for total volume of 2 mL or 1 L, as indicated. (b-d) illustrative STEM micrographs of the Au NPs obtained using (b) 2 mL, (c) 1 L, with (b) and (c) being taken at the same magnification and (d) 1 L, recorded at a different magnification. (e-f) Related size distribution for samples prepared using (e) 2 mL and (f) 1 L.

Scaling the reaction to 1 L, i.e. by a factor x500 compared to the initial screening, proved to be straightforward, as illustrated in **Figure 8**, see also **Figure S1**. Using 1 L of solution, 0.5 mM HAuCl$_4$ and a NaBH$_4$/Au molar ratio of 5, lead to NPs ca. 4-5 nm in size (4.3 ± 1.1 nm) which is the size range also obtained on a 2 mL batch (4.0 ± 1.2 nm), using the same stock solution of HAuCl$_4$ and same stock solution of NaBH$_4$. Those results confirmed the likely overlooked potential of the Au NPs simply obtained in water using only HAuCl$_4$ and NaBH$_4$, i.e. by a synthesis recipe simply implementable by experts and non-experts in nanomaterials synthesis for the benefit of the scientific community at broad.

Conclusion

The effects of HAuCl$_4$ concentration, NaBH$_4$/Au molar ratio, Additive/Au molar ratio and the use of NaCt, PVP and SDS are detailed for the NaBH$_4$-mediated colloidal synthesis of Au NPs in water at room temperature. By screening a large parameter space over 130 experiments, it is demonstrated that additives are not needed to develop stable colloidal Au NPs using this NaBH$_4$-mediated synthesis.

A fine size control over the Au NPs obtained with or without additives is easily achieved by tuning the NaBH$_4$/Au molar ratio, in particular at higher HAuCl$_4$ concentrations where larger NaBH$_4$/Au molar ratios lead to larger NPs. The use of PVP leads to the smallest NPs. There was no benefit to use NaCt or SDS compared to the surfactant-free approach. Promisingly, using PVP leads to stable small size Au NPs below 3 nm even at relatively high concentrations of ca. 3 mM HAuCl$_4$. PVP can be obtained in different grades and molecular weight which suggests additional knobs to tune further the NP properties.

The surfactant-free strategy explored here does not only lead to a simpler and more sustainable synthesis of NPs but also to nanocatalysts for water treatment or energy conversion that are more active than materials prepared by more conventional routes. The small size ca. 4-5 nm surfactant-free NPs are readily active catalysts for the 4-NP reduction but also for electrocatalysis with the examples of the EOR. The materials are anticipated to be broadly relevant for heterogeneous catalysis in water/air treatment, chemical synthesis or energy conversion.

The surfactant-free strategy conveniently performed at the relatively high concentration of 0.5 mM HAuCl$_4$ easily scales by a factor 500 in volume from 2 mL to 1 L to obtain relatively small size Au NPs around 4-5 nm. This result stresses the tractability of the method, implementable in almost any research laboratory across the globe without any prior expertise in nanomaterial synthesis. This makes the method broadly relevant for the scientific community across various disciplines. It is anticipated that the method would be relevant to develop materials for sensing, electronics and/or bio-medicine.

Altogether, the results present a solid foundation and guidelines to more rationally optimize colloidal syntheses of Au NPs and in particular to avoid the use of several unnecessary chemicals towards more sustainable preparation methods of nanomaterials and nanocatalysts. Given the widespread use of NaBH$_4$ in the synthesis of various materials, it is expected that the general principles and the achievements presented here can be applied to the preparation of a vast range of other (metal) nanomaterials for (nano)catalysis and beyond.

References

1   Heuer-Jungemann, A. *et al.* The Role of Ligands in the Chemical Synthesis and Applications of Inorganic Nanoparticles. *Chemical Reviews* **119**, 4819-4880 (2019). https://doi.org/10.1021/acs.chemrev.8b00733

2   Ateia, M. *et al.* Green and facile approach for enhancing the inherent magnetic properties of carbon nanotubes for water treatment applications. *Plos One* **12**, e0180636 (2017). https://doi.org/10.1371/journal.pone.0180636

3   Zhao, P. X., Li, N. & Astruc, D. State of the art in gold nanoparticle synthesis. *Coordination Chemistry Reviews* **257**, 638-665 (2013). https://doi.org/10.1016/j.ccr.2012.09.002

4   Rai, M., Ingle, A. P., Birla, S., Yadav, A. & Dos Santos, C. A. Strategic role of selected noble metal nanoparticles in medicine. *Critical Reviews in Microbiology* **42**, 696-719 (2016). https://doi.org/10.3109/1040841x.2015.1018131

5   Du, J., Quinson, J., Zana, A. & Arenz, M. Elucidating Pt-Based Nanocomposite Catalysts for the Oxygen Reduction Reaction in Rotating Disk Electrode and Gas Diffusion Electrode Measurements. *ACS Catalysis* **11**, 7584-7594 (2021). https://doi.org/10.1021/acscatal.1c01496

6   Duan, H. H., Wang, D. S. & Li, Y. D. Green chemistry for nanoparticle synthesis. *Chemical Society Reviews* **44**, 5778-5792 (2015). https://doi.org/10.1039/c4cs00363b

7   De Souza, C. D., Nogueira, B. R. & Rostelato, M. Review of the methodologies used in the synthesis gold nanoparticles by chemical reduction. *Journal of Alloys and Compounds* **798**, 714-740 (2019). https://doi.org/10.1016/j.jallcom.2019.05.153

8   Thanh, N. T. K., Maclean, N. & Mahiddine, S. Mechanisms of Nucleation and Growth of Nanoparticles in Solution. *Chemical Reviews* **114**, 7610-7630 (2014). https://doi.org/10.1021/cr400544s

9   Quinson, J. & Jensen, K. M. Ø. From platinum atoms in molecules to colloidal nanoparticles: A review on reduction, nucleation and growth mechanisms. *Advances in Colloid and Interface Science* **286**, 102300 (2020). https://doi.org/10.1016/j.cis.2020.102300

10   Liu, P. X., Qin, R. X., Fu, G. & Zheng, N. F. Surface Coordination Chemistry of Metal Nanomaterials. *Journal of the American Chemical Society* **139**, 2122-2131 (2017). https://doi.org/10.1021/jacs.6b10978

11   Wuithschick, M. *et al.* Turkevich in New Robes: Key Questions Answered for the Most Common Gold Nanoparticle Synthesis. *ACS Nano* **9**, 7052-7071 (2015). https://doi.org/10.1021/acsnano.5b01579

12   Rossi, L. M., Fiorio, J. L., Garcia, M. A. S. & Ferraz, C. P. The role and fate of capping ligands in colloidally prepared metal nanoparticle catalysts. *Dalton Transactions* **47**, 5889-5915 (2018). https://doi.org/10.1039/c7dt04728b

13   Mozaffari, S. *et al.* Colloidal nanoparticle size control: experimental and kinetic modeling investigation of the ligand metal binding role in controlling the nucleation and growth kinetics. *Nanoscale* **9**, 13772-13785 (2017). https://doi.org/10.1039/c7nr04101b

14   Quinson, J., Kunz, S. & Arenz, M. Surfactant-free colloidal syntheses of precious metal nanoparticles for improved catalysts. *ACS Catalysis* **13**, 4903–4937 (2023). https://doi.org/10.1021/acscatal.2c05998

15   Arminio-Ravelo, J. A. *et al.* Synthesis of Iridium Nanocatalysts for Water Oxidation in Acid: Effect of the Surfactant. *ChemCatChem* **12**, 1282-1287 (2020). https://doi.org/10.1002/cctc.201902190

16   Johnson, P., Trybala, A., Starov, V. & Pinfield, V. J. Effect of synthetic surfactants on the environment and the potential for substitution by biosurfactants. *Advances in Colloid and Interface Science* **288**, 102340 (2021). https://doi.org/10.1016/j.cis.2020.102340

17   Hutchison, J. E. The Road to Sustainable Nanotechnology: Challenges, Progress and Opportunities. *ACS Sustainable Chemistry & Engineering* **4**, 5907-5914 (2016). https://doi.org/10.1021/acssuschemeng.6b02121

18   Gilbertson, L. M., Zimmerman, J. B., Plata, D. L., Hutchison, J. E. & Anastas, P. T. Designing nanomaterials to maximize performance and minimize undesirable implications guided by the Principles of Green Chemistry. *Chemical Society Reviews* **44**, 5758-5777 (2015). https://doi.org/10.1039/c4cs00445k

19   Losch, P. *et al.* Colloidal nanocrystals for heterogeneous catalysis. *Nano Today* **24**, 15-47 (2019). https://doi.org/10.1016/j.nantod.2018.12.002

20   Handwerk, D. R., Shipman, P. D., Whitehead, C. B., Ozkar, S. & Finke, R. G. Mechanism-Enabled Population Balance Modeling of Particle Formation en Route to Particle Average Size and Size Distribution Understanding and Control. *Journal of the American Chemical Society* **141**, 15827-15839 (2019). https://doi.org/10.1021/jacs.9b06364

21   Quinson, J., Kunz, S. & Arenz, M. Beyond Active Site Design: A Surfactant-Free Toolbox Approach for Optimized Supported Nanoparticle Catalysts. *Chemcatchem* **13**, 1692-1705 (2021). https://doi.org/10.1002/cctc.202001858

22   Daniel, M. C. & Astruc, D. Gold nanoparticles: Assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chemical Reviews* **104**, 293-346 (2004). https://doi.org/10.1021/cr030698+

23   Qin, L. *et al.* "Gold rush" in modern science: Fabrication strategies and typical advanced applications of gold nanoparticles in sensing. *Coordination Chemistry Reviews* **359**, 1-31 (2018). https://doi.org/10.1016/j.ccr.2018.01.006

24   Borowskaja, D. Zur Methodik der Goldsolbereitung. *Ztschr. f. Immunitatsforsch. u. exper. Therap.* **82**, 178-182 (1934).

25   Turkevich, J., Stevenson, P. C. & Hillier, J. A study of the nucleation and growth processes in the synthesis of colloidal gold. *Discussions of the Faraday Society*, 55-75 (1951). https://doi.org/10.1039/df9511100055

26   Brust, M., Walker, M., Bethell, D., Schiffrin, D. J. & Whyman, R. Synthesis of thiol-derivatized gold nanoparticles in a 2-phase liquid-liquid system. *Journal of the Chemical Society-Chemical Communications*, 801-802 (1994). https://doi.org/10.1039/c39940000801

27   Liz-Marzan, L. M. Gold nanoparticle research before and after the Brust-Schiffrin method. *Chemical Communications* **49**, 16-18 (2013). https://doi.org/10.1039/c2cc35720h

28   Quinson, J. *et al.* Colloids for Catalysts: A Concept for the Preparation of Superior Catalysts of Industrial Relevance. *Angewandte Chemie-International Edition* **57**, 12338-12341 (2018). https://doi.org/10.1002/anie.201807450

29   Quinson, J. *et al.* Surfactant-free colloidal syntheses of gold-based nanomaterials in alkaline water and mono-alcohol mixtures. *Chemistry of Materials* **35**, 2173–2190 (2023). https://doi.org/10.1021/acs.chemmater.3c00090

30   Bizzotto, F., Quinson, J., Schröder, J., Zana, A. & Arenz, M. Surfactant-free colloidal strategies for highly dispersed and active supported IrO2 catalysts: Synthesis and performance evaluation for the oxygen evolution reaction. *Journal of Catalysis* **401**, 54-62 (2021). https://doi.org/10.1016/j.jcat.2021.07.004

31   Parveen, R., Ullah, S., Sgarbi, R. & Tremiliosi, G. One-pot ligand-free synthesis of gold nanoparticles: The role of glycerol as reducing-cum-stabilizing agent. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **565**, 162-171 (2019). https://doi.org/10.1016/j.colsurfa.2019.01.005

32   Rasmussen, D. R., Nielsen, M. F. & Quinson, J. Room Temperature Surfactant-Free Synthesis of Gold Nanoparticles in Alkaline Ethylene Glycol. *Chemistry* **5**, 900-911 (2023). https://doi.org/10.3390/chemistry5020061

33 Varga, M. & Quinson, J. Fewer, but better: on the benefits for surfactant-free colloidal syntheses of nanomaterials. *ChemistrySelect* **10**, e202404819 (2025). https://doi.org/10.1002/slct.202404819

34 Deraedt, C. *et al.* Sodium borohydride stabilizes very active gold nanoparticle catalysts. *Chemical Communications* **50**, 14194-14196 (2014). https://doi.org/10.1039/c4cc05946h

35 Quinson, J. Room Temperature Surfactant-Free Syntheses of Gold Nanoparticles in Alkaline Mixtures of Water and Alcohols: A Model System to Introduce Nanotechnology and Green Chemistry to Future Chemists and Engineers. *Journal of Chemical Education* **100**, 3612-3619 (2023). https://doi.org/10.1021/acs.jchemed.3c00492

36 Prat, D. *et al.* CHEM21 selection guide of classical- and less classical-solvents. *Green Chemistry* **18**, 288-296 (2016). https://doi.org/10.1039/c5gc01008j

37 Rodrigues, T. S. *et al.* Synthesis of Colloidal Metal Nanocrystals: A Comprehensive Review on the Reductants. *Chemistry-a European Journal* **24**, 16944-16963 (2018). https://doi.org/10.1002/chem.201802194

38 Iqbal, M. *et al.* Preparation of gold nanoparticles and determination of their particles size via different methods. *Materials Research Bulletin* **79**, 97-104 (2016). https://doi.org/10.1016/j.materresbull.2015.12.026

39 Larm, N. E., Thon, J. A., Vazmitsel, Y., Atwood, J. L. & Baker, G. A. Borohydride stabilized gold-silver bimetallic nanocatalysts for highly efficient 4-nitrophenol reduction. *Nanoscale Advances* **1**, 4665-4668 (2019). https://doi.org/10.1039/c9na00645a

40 Larm, N. *et al.* Role of Heavy Water in the Synthesis and Nanocatalytic Activity of Gold Nanoparticles. *ACS Nanoscience Au* **5**, 52-59 (2025). https://doi.org/10.1021/acsnanoscienceau.4c00069

41 Wall, M. A. *et al.* Surfactant-Free Shape Control of Gold Nanoparticles Enabled by Unified Theoretical Framework of Nanocrystal Synthesis. *Advanced Materials* **29**, 1605622 (2017). https://doi.org/10.1002/adma.201605622

42 Heo, D., Kim, K. & Kwon, S. Superior Single-Entity Electrochemistry Performance of Capping Agent-Free Gold Nanoparticles Compared to Citrate-Capped Gold Nanoparticles. *Nanomaterials* **14**, 1399 (2024). https://doi.org/10.3390/nano14171399

43 Koczkur, K. M., Mourdikoudis, S., Polavarapu, L. & Skrabalak, S. E. Polyvinylpyrrolidone (PVP) in nanoparticle synthesis. *Dalton Transactions* **44**, 17883-17905 (2015). https://doi.org/10.1039/c5dt02964c

44 Lin, C., Tao, K., Hua, D., Ma, Z. & Zhou, S. Size Effect of Gold Nanoparticles in Catalytic Reduction of p-Nitrophenol with NaBH$_4$. *Molecules* **18**, 12609-12620 (2013). https://doi.org/10.3390/molecules181012609

45 Zaheer, Z., Alsubaie, H., Kosa, S. & Aazam, E. Insights into the role of ionic surfactants on the morphology of gold and gold@silver nanoparticles. *Journal of Molecular Liquids* **400**, 124565 (2024). https://doi.org/10.1016/j.molliq.2024.124565

46 Pal, A., Shah, S. & Devi, S. Preparation of silver-gold alloy nanoparticles at higher concentration using sodium dodecyl sulfate. *Australian Journal of Chemistry* **61**, 66-71 (2008). https://doi.org/10.1071/CH07165

47 Wrigglesworth, E. & Johnston, J. The use of dual reductants in gold nanoparticle syntheses. *RSC Advances* **7**, 45757-45762 (2017). https://doi.org/10.1039/c7ra07724f

48 Ahmad, T., Wani, I., Ahmed, J. & Al-Hartomy, O. Effect of gold ion concentration on size and properties of gold nanoparticles in TritonX-100 based inverse microemulsions. *Applied Nanoscience* **4**, 491-498 (2014). https://doi.org/10.1007/s13204-013-0224-y

49 Silva, L. *et al.* Gold nanoparticles produced using NaBH$_4$ in absence and in the presence of one-tail or two-tail cationic surfactants: Characteristics and optical responses induced by aminoglycosides. *Colloids And Surfaces A-Physicochemical and Engineering Aspects* **614**, 126174 (2021). https://doi.org/10.1016/j.colsurfa.2021.126174

50   Calvin, J. J., Brewer, A. S. & Alivisatos, A. P. The role of organic ligand shell structures in colloidal nanocrystal synthesis. *Nature Synthesis* **1**, 127–137 (2022). https://doi.org/10.1038/s44160-022-00025-4

51   Cargnello, M. Colloidal Nanocrystals as Building Blocks for Well-Defined Heterogeneous Catalysts. *Chemistry of Materials* **31**, 576-596 (2019). https://doi.org/10.1021/acs.chemmater.8b04533

52   Guntern, Y. T. *et al.* Colloidal Nanocrystals as Electrocatalysts with Tunable Activity and Selectivity. *ACS Catalysis* **11**, 1248-1295 (2021). https://doi.org/10.1021/acscatal.0c04403

53   Panagopoulos, D., Asghari Alamdari, A. & Quinson, J. Surfactant-free colloidal gold nanoparticles: room temperature synthesis, size control and opportunities for catalysis. *Materials Today Nano* **29**, 100600 (2025). https://doi.org/10.1016/j.mtnano.2025.100600

54   El Amri, N. & Roger, K. Polyvinylpyrrolidone (PVP) impurities drastically impact the outcome of nanoparticle syntheses. *Journal of Colloid and Interface Science* **576**, 435-443 (2020). https://doi.org/10.1016/j.jcis.2020.04.113

55   Kuo, C., Chiang, T., Chen, L. & Huang, M. Synthesis of highly faceted pentagonal- and hexagonal-shaped gold nanoparticles with controlled sizes by sodium dodecyl sulfate. *Langmuir* **20**, 7820-7824 (2004). https://doi.org/10.1021/la049172q

56   Yuan, H. F. *et al.* Reshaping anisotropic gold nanoparticles through oxidative etching: the role of the surfactant and nanoparticle surface curvature. *RSC Advances* **5**, 6829-6833 (2015). https://doi.org/10.1039/c4ra14237c

57   Donoeva, B. & de Jongh, P. E. Colloidal Au Catalyst Preparation: Selective Removal of Polyvinylpyrrolidone from Active Au Sites. *ChemCatChem* **10**, 989-997 (2018). https://doi.org/10.1002/cctc.201701760

58   Dykman, L. A. & Khlebtsov, N. G. Methods for chemical synthesis of colloidal gold. *Russian Chemical Reviews* **88**, 229-247 (2019). https://doi.org/10.1070/rcr4843

59   Rasmussen, D. R., Lock, N. & Quinson, J. Lights on the synthesis of surfactant-free colloidal gold nanoparticles in alkaline mixtures of alcohols and water. *ChemSusChem* **18**, e202400763 (2025). https://doi.org/10.1002/cssc.202400763

60   Jæger, F., Pedersen, A. A., Wacherhausen, P. S., Smolska, A. & Quinson, J. Surfactant-free gold nanoparticles synthesized in alkaline water-ethanol mixtures: leveraging lower grade chemicals for size control of active nanocatalysts. *RSC Sustainability, 3,* 2870-2875 (2025). https://doi.org/10.1039/D5SU00213C

61   Liz-Marzan, L. M., Kagan, C. R. & Millstone, J. E. Reproducibility in Nanocrystal Synthesis? Watch Out for Impurities! *ACS Nano* **14**, 6359-6361 (2020). https://doi.org/10.1021/acsnano.0c04709

62   Roy, A. *et al.* The Huge Role of Tiny Impurities in Nanoscale Synthesis. *ACS Nanoscience Au* **4**, 176-193 (2024). https://doi.org/10.1021/acsnanoscienceau.3c00056

63   Jensen, T., Saugbjerg, J., Henriksen, M. & Quinson, J. Towards the automation of nanoparticle syntheses: The case study of gold nanoparticles obtained at room temperature. *Colloids and Surfaces A-Physicochemical And Engineering Aspects* **702**, 135125 (2024). https://doi.org/10.1016/j.colsurfa.2024.135125

64   Reichenberger, S., Marzun, G., Muhler, M. & Barcikowski, S. Perspective of Surfactant-free Colloidal Nanoparticles in Heterogeneous Catalysis. *ChemCatChem* **11**, 4489-4518 (2019). https://doi.org/10.1002/cctc.201900666

65   Zhao, P., Feng, X., Huang, D., Yang, G. & Astruc, D. Basic concepts and recent advances in nitrophenol reduction by gold- and other transition metal nanoparticles. *Coordination Chemistry Reviews* **287**, 114-136 (2015). https://doi.org/10.1016/j.ccr.2015.01.002

66   Neal, R., Inoue, Y., Hughes, R. & Neretina, S. Catalytic Reduction of 4-Nitrophenol by Gold Catalysts: The Influence of Borohydride Concentration on the Induction Time. *Journal of Physical Chemistry C* **123**, 12894-12901 (2019). https://doi.org/10.1021/acs.jpcc.9b02396

67   Cerimedo, M., Baronio, L., Hoppe, C. & Ayude, M. The Effect of Poly(vinylpyrrolidone) (PVP) on the Au Catalyzed Reduction of p-nitrophenol: The Fundamental Role of NaBH$_4$. *ChemistrySelect* **4**, 608-616 (2019). https://doi.org/10.1002/slct.201803250

68   Al-Johani, H. *et al.* The structure and binding mode of citrate in the stabilization of gold nanoparticles. *Nature Chemistry* **9**, 890-895 (2017). https://doi.org/10.1038/nchem.2752

69   Quinson, J., Nielsen, T. M., Escudero-Escribano, M. & Jensen, K. M. Ø. Room temperature syntheses of surfactant-free colloidal gold nanoparticles: the benefits of mono-alcohols over polyols as reducing agents for electrocatalysis. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **675**, 131853 (2023). https://doi.org/10.1016/j.colsurfa.2023.131853