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$NaBH_4$-mediated syntheses of colloidal gold nanocatalysts in water: are additives really needed?

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Nanomaterials are relevant for several applications in electronics, sensing, biomedicine, optics, and catalysis, among other fields. As a consequence, a wide range of colloidal syntheses have been reported in which a precursor is reduced to metallic nanoparticles (NPs). In numerous protocols, stabilizers such as surfactants are added to ensure colloidal stability and/or to 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), polyvinylpyrrolidone (PVP) or sodium dodecylsulfate (SDS), in the fast (seconds-long) room temperature synthesis of gold (Au) NPs obtained otherwise using only water and $NaBH_4$ in its surfactant-free version. The effects of the $NaBH_4$/Au molar ratio, additive/Au molar ratio and concentration of $HAuCl_4$ used as a precursor are jointly investigated in a parametric study of over 130 samples. The influence of the order of the addition of the chemicals is also discussed. It is found that there is no benefit in using additives for size control, stability or catalysis. Control over the NP size in the range of 3–10 nm is easily achieved without additives by controlling the $NaBH_4$/Au molar ratio. A benefit of PVP is that it leads to NPs smaller than 3 nm even at a relatively high concentration of $HAuCl_4$ 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 that are stable over time but also to lead, in most cases, to catalysts as active as or even more active than the NPs prepared with additives. This is exemplified by the 4-nitrophenol reduction, a model reaction for water treatment, and by the electrocatalytic ethanol oxidation reaction (EOR), 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 of 500 compared with the parametric study performed. Overall, the results demonstrate the benefits of surfactant-free approaches to develop gold-based nanomaterials and provide guidelines to optimize their synthesis towards more sustainable nanotechnologies.

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1 Introduction

Due to their unique size, morphology and composition-dependent properties, nanomaterials offer a wide range of opportunities for applications in electronics, medicine, sensing, catalysis, water/air treatment and more.[1–5] The optimized use of a nanomaterial requires careful syntheses. Several synthetic methods have been reported and largely exploited to prepare various nanoparticles (NPs).[6,7] In particular, colloidal NPs prepared in the liquid phase by the 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, or protective agents are reported to be required to achieve successful syntheses of NPs and to control NP size, stability and/or crystal structure.[1,10–14] Although these additives can help obtain 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, these additives are often derived from fossil fuels;[16] thus, they are not optimal to holistically address sustainability, environmental matters and green chemistry, which would require the NP syntheses to be more sustainable in the first place,[17,18] regardless of the application.

Nanomaterial 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.[7,21] In other words, it remains unclear which chemicals are truly and minimally needed to achieve a given outcome. As a consequence, the effect of the preparation

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methods and the choice of a stabilizer on the resulting properties of the NPs is also relatively poorly studied. There is a lack of 'control' experiments or 'blank' samples in which a successful synthesis is achieved in the first place without 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.[14,22]

In particular, Au NPs are a widely studied class of materials due to their biocompatibility, plasmonic and catalytic properties.[23,24] Various colloidal syntheses of Au NPs have been reported, where the most iconic is probably the Borowskaja-Turkevich-Frens method,[11,25,26] performed in water close to the boiling point using citrate as a reducing and stabilizing agent, or the Brust-Schiffrin method using $NaBH_4$ as reducing agent and thiol molecules as stabilizers.[27,28] 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 in which no chemical other than the metal precursor has a molar mass higher than 100 g mol^{-1}, as detailed elsewhere.[14] In other words, only relatively small-sized molecules or charged species play the role of stabilizers. Several methods lead to surfactant-free colloids and include plasma-,[29] laser-,[30] DMF-,[31] alcohol-,[32] and water-mediated[33] syntheses. The last two methods are specifically promising because they do not require specific equipment, involve only relatively safe processes and chemicals, and do not require specific knowledge *a priori*; thus, they have the potential to be widely implemented.

In the quest to understand and optimize colloidal syntheses, in particular to by-pass the challenges of so-called one-pot syntheses of supported nanomaterials detailed elsewhere,[14,22] we showed that various surfactant-free colloidal syntheses of metal NPs can be developed in alcohol/water-based solvents.[22,34–36] 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.[37] We showed that glycerol can be substituted with ethylene glycol[38] or ethanol[35] to develop more sustainable syntheses in solvents with low(er) boiling points. 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.[39] Actually, using additives resulted in lower stability and/or larger NPs in most cases.

Although these surfactant-free approaches might not lead to the most monodispersed samples or the most fine control over the NP structure or the most stable materials, they lead to production methods requiring few chemicals with the potential to be easily implemented by non-experts,[33,40] which is promising for real-life production and implementation.[14,34,35] Furthermore, due to their relatively free surface, these surfactant-free approaches tend to lead to nanocatalysts with higher catalytic activity than the state of the art.[33–35]

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 noting that this method presents the advantage of requiring only water as a green solvent,[41] 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.[42] Astruc and co-workers showed that when $NaBH_4$ is used as a reducing agent, there is no need for any other chemicals to obtain stable colloidal NPs.[33] A similar approach was used by Iqbal *et al.*,[43] or Elnagar *et al.*,[44] to prepare Au NPs as well as by Larm *et al.* to prepare Au_xAg_{1-x} NPs;[45,46] see details in Table S1 in the supporting information (SI). Other researchers demonstrated the relevance of the approach to obtain Ru,[47] Pt[48] or Pd[49] nanomaterials, among other metals.[50] Nevertheless, a much wider range of syntheses and a body of literature, including $NaBH_4$-mediated syntheses of Au NPs, still prefer and report the use of commercially available citrate (NaCt),[11,51,52] polyvinylpyrrolidone (PVP)[53,54] or sodium dodecylsulfate (SDS).[55,56] Other reported chemicals, among many options, could be tannic acid,[57] ascorbic acid,[57] tritonX[58] or CTAB,[59] or synthesized additives.[44]

Here, we first aim to investigate the actual need and potential benefits for various additives (none, NaCt, PVP, and SDS) in $NaBH_4$-mediated syntheses of Au NPs in water for various $HAuCl_4$ precursor concentrations (0.1, 0.2, and 0.5 mM), various $NaBH_4$/Au molar ratios (5, 8, and 10) and various additives/Au molar ratios (0, 5, 10, and 15) when it comes to size control and stability of the NPs. These values and chemicals were selected as representatives of those commonly used in various protocols in the literature and to cover a broad parameter space, as detailed in the SI in the experimental section.

A first goal is to question the actual need for such chemicals and identify a strategy to develop more sustainable syntheses. Second, 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, which is almost systematically found in the literature, that additives are needed to develop successful syntheses of colloidal Au NPs.[14,60,61] 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 the size control and stability of as-prepared colloidal Au NPs and for their catalytic properties for the 4-nitrophenol (4-NP) reduction and ethanol oxidation reaction (EOR).

2 Scope

Although control over NP properties across a broad size range is ultimately a general goal[61,62] to facilitate the discussion below, it is here considered that a synthesis is optimal if (i) it leads to small size NPs (more likely to be stable and relevant for catalysis since smaller Au NPs tend to be more active[63]); (ii) it requires few chemicals (ultimately leading to a process simpler, cheaper and less sensitive to contamination[64]); (iii) it requires a low amount of chemicals (ultimately cheaper, more likely to scale up, in line with the principles of green and sustainable chemistry[6]); (iv) it can be performed at high $HAuCl_4$ concentration (because a lower volume of solvent is required to produce a given amount of Au NPs).

A wide range of additives can be used in $NaBH_4$-mediated syntheses. Here, NaCt was selected owing to its wide use as a stabilizing agent in Au NP syntheses.[11,52] NaCt can also play the role of a reducing agent,[42] but the synthesis is poorly controlled at room-temperature if $NaBH_4$ is not used. In general, PVP was selected for its wide use in Au NP synthesis and NPs in general.[53] PVP, a non-ionic polymer, can also play the role of a reducing agent,[42] 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.[56,65] Other common additives, such as tannic acid and ascorbic acid, were excluded due to their relatively strong reducing properties.[57] CTAB is another widely used chemical in Au nanomaterial syntheses.[59,66] However, these chemicals are relatively harmful and would ideally be avoided to develop a synthesis method compatible with the principles of green and sustainable chemistry in nanoscience.[6,17] For similar reasons, water is preferred as a solvent although $NaBH_4$-mediated syntheses have been reported in alternative solvents, such as methanol.[67]

It is to be expected that alternative solvents and chemicals may be relevant to study beyond the examples proposed below in this first report for a deeper understanding of Au NPs and the development of (even more) sustainable syntheses.

3 Experimental

Extensive details on the Au NP syntheses, their characterization, procedures followed and metrics retrieved for the catalytic assessments are provided in the SI. In particular, UV-vis measurements and the metrics retrieved together with their significance are detailed in Table S2. The general synthesis methods follow an approach reported by Astruc and co-workers with modifications.[33] The samples considered for this study are illustrated in Table S3.

4 Results and discussion

4.1. General synthesis concept

The addition of $NaBH_4$ 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 with a diameter of approximately 5 nm. The reaction proceeds without or with additives. An illustration of the synthesis process, together with illustrative UV-vis and STEM data are shown in Fig. 1. Illustrative XRD data confirming the formation of fcc Au NPs are shown in Fig. S2.

4.2. Parametric study

First, the effects of using or not using various additives at the same 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 Fig. 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 that in previous reports[33,45] because a finer $NaBH_4$/Au molar ratio is screened; here, the influence of the $HAuCl_4$ concentration is also considered.

For 0.1 mM $HAuCl_4$, the sizes for $NaBH_4$/Au molar ratios of 5, 8, and 10 are 4.7 ± 0.9 nm, 4.4 ± 0.8 nm, and 4.8 ± 0.9 nm, respectively, for λ_{spr} values of 510, 510, and 510 nm, and A_{spr}/A_{450} values of 1.23, 1.21, and 1.24, respectively. For 0.2 mM $HAuCl_4$, the sizes for $NaBH_4$/Au molar ratios of 5, 8, and 10 are 4.0 ± 0.8 nm, 4.4 ± 1.3 nm, and 4.8 ± 0.9 nm, respectively, for λ_{spr} values of 508, 514, and 512 nm, and A_{spr}/A_{450} values of 1.17, 1.27, and 1.26, respectively. For 0.25 mM $HAuCl_4$, the sizes for $NaBH_4$/Au molar ratios of 5, 8, and 10 are 5.5 ± 2.1 nm, 4.4 ± 1.2 nm, and 5.2 ± 1.3 nm, respectively, for λ_{spr} values of 514, 510, and 514 nm, and A_{spr}/A_{450} values of 1.26, 1.27, and 1.29, respectively. For 0.50 mM $HAuCl_4$, the sizes for $NaBH_4$/Au molar ratios of 5, 8, and 10 are 4.1 ± 1.2 nm, 6.5 ± 1.3 nm, and 10.0 ± 3.5 nm, respectively, for λ_{spr} values of 515, 515, and 520 nm, and A_{spr}/A_{450} values of 1.31, 1.43, and 1.61, respectively.

To date, all studies related to the surfactant-free $NaBH_4$-mediated synthesis of Au NPs have been performed at a fixed concentration of $HAuCl_4$, see Table S1. 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 using the same concentrations 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 when it comes to size control.

For instance, the use of 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 of 4.8 ± 0.9, 4.0 ± 0.8 and 3.8 ± 0.7 nm for the first three experiments, respectively, and unstable NPs of greater than 50 nm in the last case. The use of 0.20 or 0.25 mM and 2.00 mM $NaBH_4$ ($NaBH_4$/Au molar ratios of 10 and 8, respectively) leads to NP sizes of 4.8 ± 0.9 nm and 4.4 ± 1.2 nm, respectively. The use of 0.50, 0.25 and 2.50 mM $NaBH_4$ ($NaBH_4$/Au molar ratios of 5 and 10, respectively) leads to NP sizes 4.1 ± 1.2 nm (4.0 ± 0.8 nm on a repeat) and 5.2 ± 1.3 nm, respectively. There is therefore 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.

4.3. Effects of additives

The trend that higher λ_{spr} values, related to larger NPs, as illustrated in Fig. S3, are obtained when the $NaBH_4$/Au molar ratios increase, is also observed in the presence of various

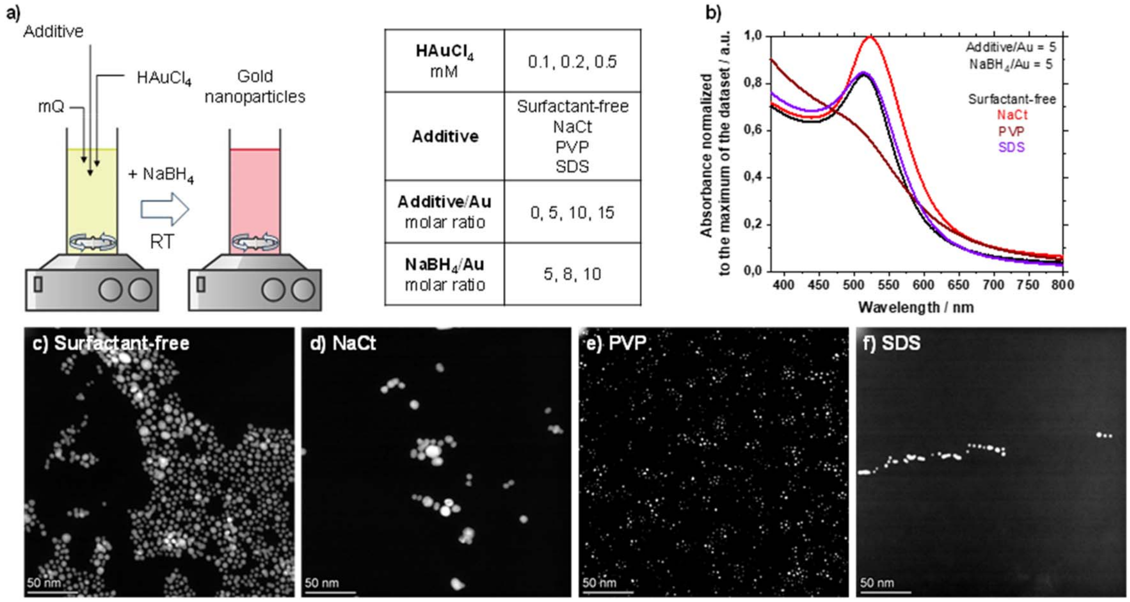

Fig. 1 (a) Schematic of the $NaBH_4$-mediated synthesis of Au NPs at room temperature. Created with Chemix (2025), retrieved from https://chemix.org and adapted. RT stands for room temperature. (b) Illustrative UV-vis and (c–f) STEM micrographs of the Au NPs obtained (c) without additives, (d) with NaCt, (e) PVP, and (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) is due to contamination from SDS, which interacts with the high-energy beam of the microscope.

additives (NaCt, PVP, and SDS) at different ratios, as shown in Fig. S4. This trend is in line with previous reports,[44] where a fixed concentration of additive was typically used and/or a support, such as Al_2O_3. For instance, the use of 0.6 mM $HAuCl_4$, a PVP/Au molar ratio of 1.5 and $NaBH_4$/Au molar ratios of 6.7, 8.3, 16.7, and 18.3 led to sizes of 1.7, 3.4, 5.7 and 8.2 nm, respectively.[54] The larger NPs obtained can be attributed to the presence of more reducing agents, leading to a more pronounced growth of the NPs.[33,44]

The use of different additives leads to different sizes, as illustrated in Fig. 2b, with 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 ratios are shown in Fig. S5. The trend is that the use of NaCt leads to dispersions characterized by higher λ_{spr} values, indicating larger NPs, compared with the surfactant-free approach. PVP leads to very small NPs with almost no SPR feature, compared with the surfactant-free approach. The use of SDS does not lead to any benefit compared with the surfactant-free approach. Interestingly, the use of PVP leads to stable and small-sized (<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 and PVP can play the role of reducing agents.[42] 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 with surfactant-free NPs.

For a given additive, there is a trend to observe larger NPs as the amount of additive increases. This is, for instance, illustrated in Fig. 2c with the example of NaCt and a $NaBH_4$/Au molar ratio of 5. These results also illustrate the negative effect of higher concentrations of additives, leading to unstable colloids, especially at higher $HAuCl_4$ concentrations, as illustrated in Fig. S6. A decrease in stability at higher $HAuCl_4$ concentrations is not observed or is slightly observed in the surfactant-free approach. At too high concentrations of additives, additive–additive interactions might also lead to the formation of larger NP aggregates, which can account for the lower colloidal stability under these conditions. In particular, the use of NaCt leads to unstable colloids characterized by overall low absorption in UV-vis measurements, see Fig. 2c. The same tends to occur with SDS although the effect is relatively less pronounced.

4.4. 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,[7,11,68] adding the $HAuCl_4$ last (often referred to as *inverse* or *reverse* conditions, as opposed to direct conditions where the NaCt is added last) leads to narrower size distributions. A similar observation was made for ethanol-mediated synthesis under alkaline conditions, where the outcome of the synthesis also depends on the concentration of the stock solution of $HAuCl_4$.[35] In a nutshell, a finer size control is obtained in this last case when the gold is in its acid form, which is more likely to be reduced. This can be

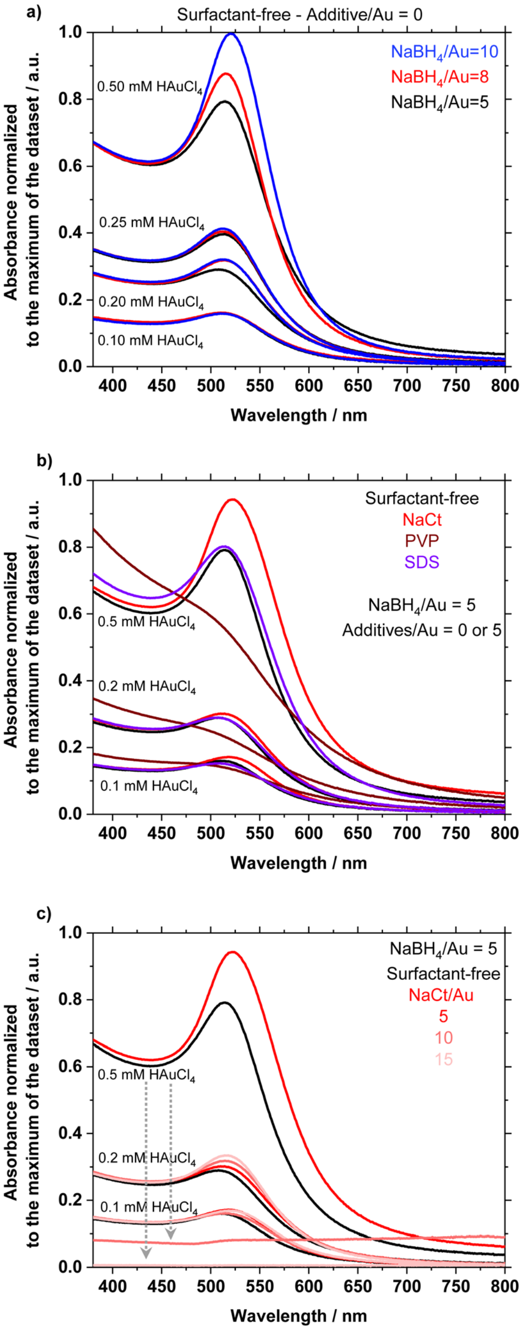

Fig. 2 UV-vis spectra illustrating the effect of various variables on the synthesis of Au NPs using a room temperature $NaBH_4$-mediated approach. (a) Effect of $HAuCl_4$ concentration and $NaBH_4$/Au molar ratio on a surfactant-free synthesis. (b) Effect of using different additives, as indicated. (c) 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. The related STEM data and analysis are given in Fig. S8.

achieved by adding a concentrated solution of $HAuCl_4$ to neutral or alkaline conditions such that the gold is ‘locally’ in its acid form.

Here, we did not observe a strong effect of the order of the addition of the chemicals in the $NaBH_4$-mediated surfactant-free synthesis of Au NPs. We also assessed whether 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. These 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 these conditions and especially not for the surfactant-free version, see UV-vis data in Fig. S7 and STEM data together with the related analysis in Fig. S9. The little dependence on the direct or inverse method is attributed here to the strong reducing properties of $NaBH_4$, which leads to a reduction in seconds.

4.5. 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,[69] grade of chemicals[70] and many other ‘impurities’.[71,72] The use of additives from different suppliers and/or with different grades can also account for the lack of reproducibility.[64] In the present case, the main source of irreproducibility might be from the fact that the solution of $NaBH_4$ is preferentially prepared fresh; therefore, slightly different concentrations of the stock solution might be used across the same study.

In order to best assess reproducibility, we reproduced the conditions of 0.5 mM $HAuCl_4$ and a $NaBH_4$/Au molar ratio of 5 several times on different days using different stock solutions of $NaBH_4$, 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 Fig. S7. The results suggest a relatively robust synthesis in the case where a surfactant-free approach is developed or when PVP is used.

4.6. Optimization

The present study screens a relatively larger parameter space compared with most previous reports.[33,45,73] The incentive here was not to ‘optimize’ the synthesis. Rather, the trends reported here should be observed as guidelines for finer optimization in 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 lead 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 observed experimentally, as illustrated in Fig. 3a, where using a NaCt/Au molar ratio of 1 is the only case that leads to NPs with a lower λ_{spr} value with only a slightly smaller size compared with the surfactant-free approach, Fig. 3b. Complementary STEM data and the related analysis are provided in Fig. S10. This example shows how the present results can be used as a foundation for the selection of the additives in the desired concentrations for a 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.

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

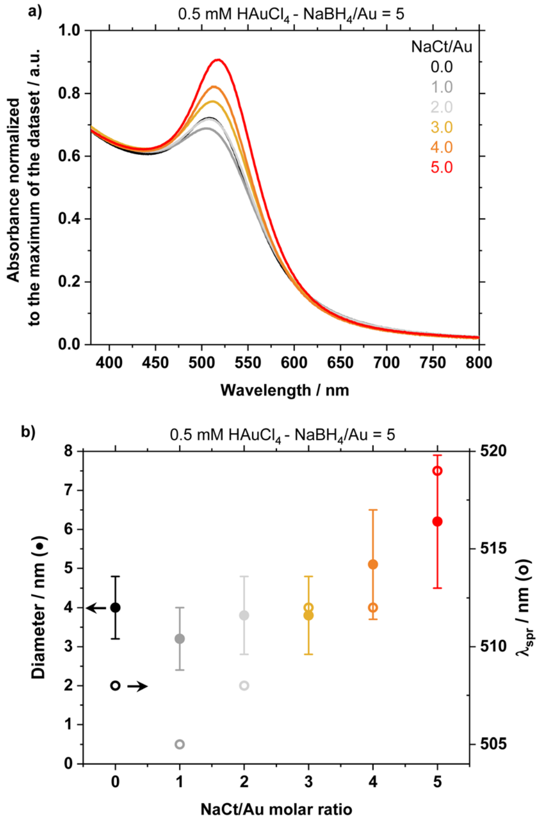

Fig. 3 (a) UV-vis spectra of the Au NPs prepared with various NaCt/Au molar ratios, as indicated. (b) Diameter (●, left-hand side axis) and λ_{spr} values (o, right hand–side axis) for the Au NPs obtained with various NaCt/Au molar ratios, as indicated. In all cases, 0.5 mM HAuCl$_4$ and a NaBH$_4$/Au molar ratio of 5 were used. STEM micrographs and size distributions are illustrated in Fig. S10.

illustrated in Fig. 4a, indicating small size NPs of around 3 nm or below. This observation encourages scaling up the reaction. Most colloidal syntheses of Au NPs are performed in the 0.1–0.5 mM range of a 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 led us to select conditions where relatively small amounts of chemicals were used, *i.e.* NaBH$_4$/Au molar ratio of 5 and PVP/Au molar ratio of 5, but where the HAuCl$_4$ concentrations were 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$_4$. The results are presented in Fig. 4. The lower overall absorption decreases for higher HAuCl$_4$ concentrations of 4–5 mM, indicating less stable NPs. The diameter of the NPs tends to increase with an increasing concentration of HAuCl$_4$, as illustrated in Fig. 4a, but the NPs remain below 3 nm in diameter, as illustrated in Fig. 4b. See also Fig. S11 for complementary STEM data and related analysis.

Equally, since a PVP/Au molar ratio of 5 leads to very small Au NPs, and no PVP leads to relatively small size yet larger NPs, there is probably room for finer size control. We therefore investigated PVP/Au molar ratios from 0.1 to 5.0, as detailed in entries 117–138 in Table S1. Based on UV-vis data reported in Fig. 4c, and STEM data analysis reported in Fig. 4d, further detailed in Fig. S12, 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.

4.7. 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 of guaranteeing the stability of the colloids. In our experience with surfactant-free syntheses and as detailed by others, this is not required.[30,39] The stability of the colloids was 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), and 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 observe slightly higher A_{spr} values as illustrated in Fig. S13–S16.

4.8. Catalysis

Having established that various additives lead to different size controls over 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 a well established catalytic reaction relevant to benchmark Au NPs and a model reaction for water treatment.[33,74] The use of NaBH$_4$-mediated syntheses of Au NPs is particularly relevant for this reaction, which typically requires an excess of NaBH$_4$.[33,75] We also considered the EOR as a model reaction for electro-catalysis and relevant for energy conversion.[63] 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 of using different additives in the synthesis of Au NPs. In particular, a pending question is whether 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, are added as the Au NPs are used for catalysis. A range of approaches have been reported to clean 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.[34] Our focus here

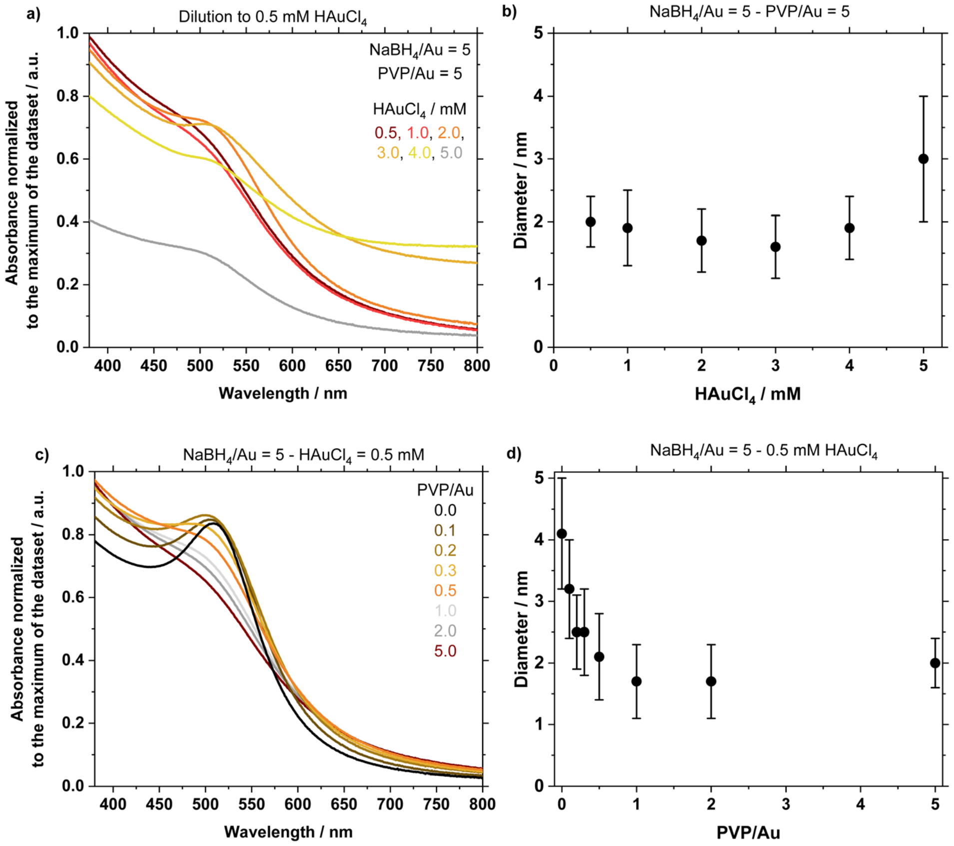

Fig. 4 (a) UV-vis spectra of the Au NPs prepared with various $HAuCl_4$ concentrations, as indicated, a PVP/Au molar ratio of 5 and a $NaBH_4$/Au molar ratio of 5. For measurements, all samples were diluted to 0.5 mM equivalent of Au. (b) Corresponding diameter of the Au NPs, as indicated. (c) UV-vis spectra of the Au NPs prepared with various PVP/Au molar ratios, 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 depicted in Fig. S12.

is on the strategy that develops readily active materials, without the need for extra washing or additive removal that could significantly contribute to bridging the gap between fundamental and applied research.[14,19,34]

4.8.1. 4-NP reduction. When the 4-NP reduction is followed by UV-vis catalyzed by Au NPs, as illustrated in Fig. 5a, the use of different NPs obtained using no additives, NaCt, PVP or SDS leads to some degree of catalytic activity, as illustrated in Fig. 5b, see also Fig. S17. The most active catalysts characterized by the highest k_{app} values (see SI for details) and highest TOF values are obtained using the NPs prepared without additives, see Fig. 5c and S18. 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 surfactant-free NPs are more active, which can be explained by their more accessible surface resulting from the use of $NaBH_4$ only (without additives) during the synthesis, as well as the fact that $NaBH_4$ is also used here in large excess for catalytic reduction. $NaBH_4$ was also shown to be a suitable reagent to clean NP surfaces, and this probably explains the relatively high activity of the Au NPs prepared using SDS and PVP,[67,76] while the efficiency of this cleaning effect might be more moderate for Au NPs prepared using NaCt.

Another important factor to consider is the size of the NPs. It is expected that the smallest NPs should lead to the most active catalysts.[63] 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, while 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 using a surfactant-free approach can be attributed to the absence of additives. The Au NPs prepared using 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 in the case of the use of NaCt.[77]

An interesting case is the Au NPs prepared using PVP, which are the smallest NPs. Thus, it would be expected that their activity would be significantly higher than that of other Au NPs. However, a small size is here achieved using PVP, which is known to interact rather strongly with the Au NP surface[35] and therefore block the active sites. The relatively high activity observed here is attributed to the small size of the Au NPs, which 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

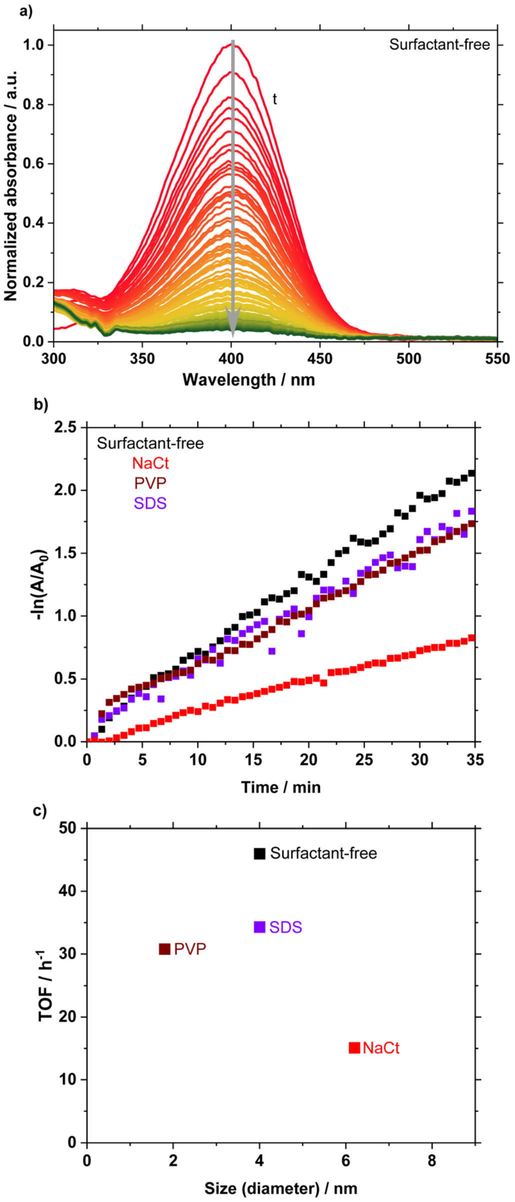

Fig. 5 (a) Illustration of 4-NP reduction in the presence of $NaBH_4$ catalyzed by surfactant-free Au NPs normalized to the maximum of the dataset. (b) Plot of $-\ln(A/A_0)$ as a function of time used to retrieve the k_{app} values for 4-NP catalyzed by Au NPs prepared using a surfactant-free approach with NaCt, PVP or SDS, as indicated. (c) TOF values as a function of NP size. More details are available in Section 8 of the SI, including TOF values normalized by the A_{400} values retrieved from UV-vis for the Au NP dispersions, as illustrated in Fig. S18.

regarding the Au NPs prepared using PVP are therefore attributed to a balance between a small size (favouring a higher activity), the presence of an excess of $NaBH_4$ (favouring a higher activity by cleaning the NP surface), and the use of PVP (promoting a lower activity).

Overall, these results illustrate the importance of designing catalytic materials beyond active sites and tailoring the features of a desirable catalyst as much as possible during synthesis, for example, by developing or considering surfactant-free Au NPs. In this respect, the results show that there is no benefit to using 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 ref. 78, and the references therein. It must be kept in mind that the focus here is 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.[70] The TOF values obtained here agree well with previous preliminary results from our group using the surfactant-free $NaBH_4$-mediated synthesis of Au NPs.[70] In particular, in our previous study, 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.[70] The *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.

4.8.2. Ethanol oxidation reaction (EOR). To the best of our knowledge, the potential benefits of colloidal surfactant-free Au NPs prepared using only $NaBH_4$, water and $HAuCl_4$ prepared without support have not been detailed for any other reactions except for the 4-NP reduction.[33,45] A range of other heterogeneous catalytic processes 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 under 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 using 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 depicted in Fig. 6, such as electrochemically active surface area (ECSA) in Fig. 6a, mass activity (MA) in Fig. 6b, or MA after an acidic treatment (MA_{acid}) in Fig. 6c. All parameters and definitions are detailed in SI, particularly in Subsection 2.9. A typical cyclic voltammogram for the EOR[63] is illustrated in Fig. 7 and in S19. 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.[63] Supplementary 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 Fig. S20–S23 with complementary data in Fig. S24.

Using no additive, NaCt, PVP or SDS leads to relatively active materials (every parameter being kept constant, black, red, brown and purple data points). The ECSA of the samples satisfies the following trend: surfactant-free ≈ NaCt > SDS >> PVP. The activity (MA) follows the trend: surfactant-free > NaCt >

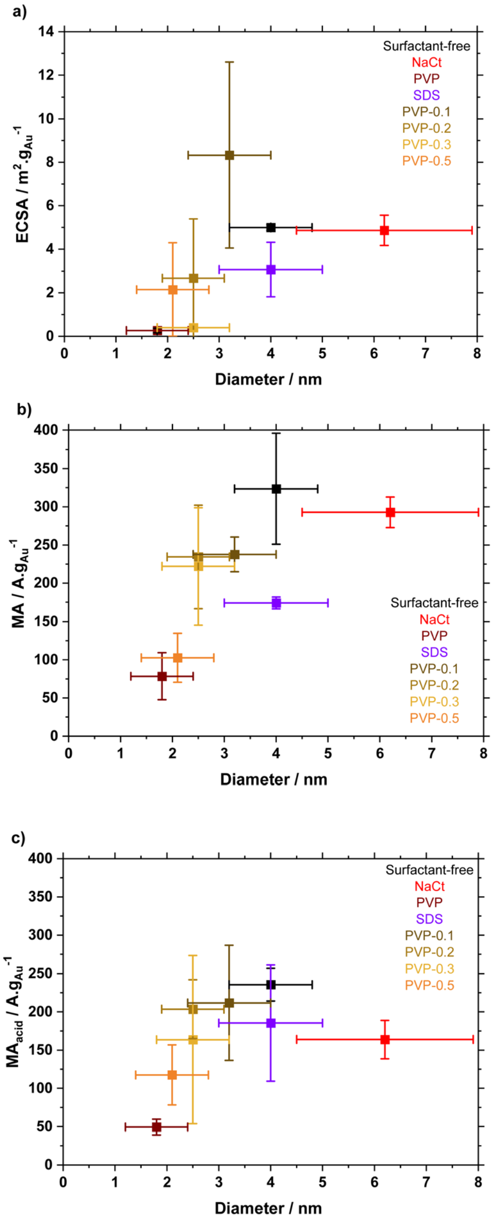

Fig. 6 (a) ECSA, (b) MA and (c) MA plots after an acidic treatment for the samples prepared without additives, with NaCt, with PVP (with various PVP/Au molar ratios of 0.1, 0.2, 0.3 or 0.5) or SDS, as indicated. Unless otherwise specified, the Au NPs were prepared using 0.5 mM $HAuCl_4$, $NaBH_4$/Au 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.

SDS >> PVP. This trend is also observed when the Au NPs are subjected to acid treatment (MA_{acid}), with an overall decrease in the MA values, which is attributed to the loss of Au NPs by dissolution during the oxidation-reduction process at stake during the acid step used to evaluate the ECSA. The MA_{acid} satisfies the following trend: surfactant-free > NaCt ≈ SDS >> PVP.

There is no strong relationship between the measured values 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.[63] 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.

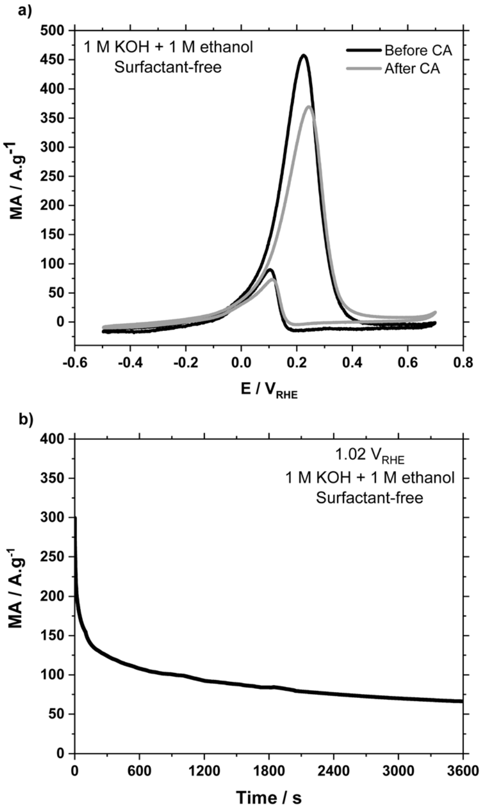

Fig. 7 (a) CV plots of Au NPs obtained using a surfactant-free $NaBH_4$-mediated synthesis using 0.5 mM $HAuCl_4$, a $NaBH_4$/Au molar ratio of 5 before and after CA at 1.02 V_{RHE} in 1 M KOH and 1 M ethanol, recorded at a scan rate of 50 mV s^{-1}. The 10th scan is represented. (b) CA plot at 1.02 V_{RHE} in 1 M KOH and 1 M ethanol.

Given that the NPs with the smallest sizes are expected to lead to more active NPs, and given that an increasing amount of PVP leads to significantly smaller NPs compared with surfactant-free NPs, we assessed whether an optimal PVP amount leading 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, Fig. 6a, there was no benefit to using any PVP compared with the surfactant-free version of the Au NP $NaBH_4$-mediated synthesis, where the MA was in the same range or lower compared with 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 depicted in Fig. 7. A decrease in activity is observed over time, as

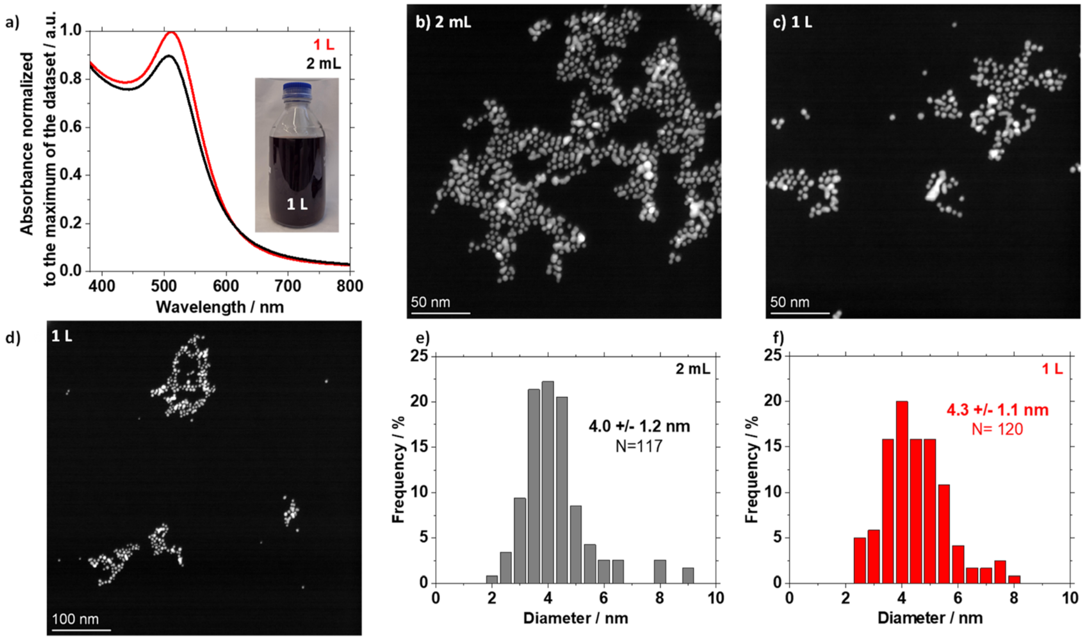

Fig. 8 (a) UV-vis spectra of the Au NPs prepared using a surfactant-free $NaBH_4$-mediated colloidal synthesis using 0.5 mM $HAuCl_4$ and a $NaBH_4$/Au molar ratio of 5, for a total volume of 2 mL or 1 L, as indicated. (b–d) Illustrative STEM micrographs of the Au NPs obtained using (b) 2 mL, (c) 1 L, recorded at the same magnification and (d) 1 L, recorded at a different magnification. (e–f) Related size distribution for the samples prepared using (e) 2 mL and (f) 1 L.

shown in Fig. 7b, but the activity can be recovered as shown in the cyclic voltammograms of Fig. 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.[79]

The electrochemical tests performed are convenient for the first relative comparison of the materials. It can be expected that the differences observed might not translate to other testing protocols using different conditions or setups, such as rotating disk electrode (RDE), gas diffusion electrode (GDE), or membrane electrode assembly (MEA).[80] Nevertheless, these experiments provide a first important insight into the fact that additives are not required to develop active catalysts.

4.8.3. Comparison with catalysts prepared using other surfactant-free strategies. The comparison of the catalytic activity of NPs obtained using different surfactant-free approaches is almost not reported and constitutes a gap in the literature.[14] This is in great part due to the need to obtain samples by applying different techniques requiring various equipment and expertise (*e.g.* for laser- and plasma-mediated approaches). It is therefore interesting to compare the results obtained here for Au NPs prepared by a surfactant-free $NaBH_4$-mediated synthesis with 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 with the surfactant-free $NaBH_4$-mediated synthesis studied here. Although the Au NPs prepared by an ethanol-mediated synthesis show a size of around 10 nm, the NPs achieved a TOF of around 50–70 h^{-1}.[70] For the EOR, the ethanol-mediated synthesis leads to Au NPs with relatively high MAs of around 300 A g_{Au}^{-1},[63] *i.e.* MAs close to those obtained here (MA around 325 A g_{Au}^{-1}) with *ca.* 5 nm NPs. In other words, the activity increase by achieving surfactant-free Au NPs *via* a $NaBH_4$-mediated synthesis is not as pronounced as the significant size decrease expected (given that the NP size is divided by *ca.* 2 from an ethanol-mediated to a $NaBH_4$-mediated surfactant-free synthesis).

Just as in the case of the 4-NP reduction, although it is beyond the scope of this report to clarify the reason behind this observation, these results demonstrate 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 in developing 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.[14,22]

4.9. 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 4-NP reduction was suggested. It is shown here 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 shown here 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 that are also relevant for electrocatalysis, with the example of the EOR.

These results highlight the potential of the small-sized NPs rapidly obtained with simple equipment for heterogeneous catalysis and other areas of application. A challenging aspect of most colloidal NP syntheses is their limited scalability, often related to the need to use specific equipment, which makes it challenging to successfully prepare 'large batches'. The present approach has the potential to bypass this bottleneck. Previous studies focused on 33 mL for 0.13 mM_{Au} (*ca.* 0.8 mg_{Au} per batch)[33] or 0.25 mM_{Au} for 20 mL (*ca.* 1 mg_{Au} per batch)[45,46] or 0.25 mM for *ca.* 100 mL (*ca.* 5 mg_{Au} per batch),[43] see Table S1. Since our optimization was performed on a small volume of solution for each sample (2 mL), and given that a larger amount of NPs would be required for further use, we investigated the possibility of scaling up the synthesis to 1 L for a relatively high concentration of 0.5 mM $HAuCl_4$. This would lead to *ca.* 100 mg_{Au} per batch, which is a more suitable quantity for a range of catalytic testing and further use of the NPs.

Scaling the reaction to 1 L, *i.e.* by a factor of 500 compared with the initial screening, proved to be straightforward, as illustrated in Fig. 8, see also Fig. S2. 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 the same stock solution of $NaBH_4$. These 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 nanomaterial synthesis for the benefit of the scientific community at large.

5 Conclusions

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 for over 130 experiments, it is demonstrated that additives are not needed to develop stable colloidal Au NPs using this $NaBH_4$-mediated synthesis.

Size control over the Au NPs obtained with or without additives is easily achieved by tuning the $NaBH_4$/Au molar ratio, particularly 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 using NaCt or SDS compared with the surfactant-free approach. Promisingly, using PVP leads to stable small-sized 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 weights, suggesting additional knobs to further tune NP properties.

The surfactant-free strategy explored here not only leads 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 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 of 500 in volume from 2 mL to 1 L to obtain relatively small-sized Au NPs around 4–5 nm. This result stresses the tractability of the method, which is implementable in almost any research laboratory across the globe without any prior expertise in nanomaterial synthesis. This makes the method broadly relevant to 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,[47–49] it is expected that the general principles and achievements presented herein can be applied to prepare a vast range of other (metal) nanomaterials for (nano)catalysis and beyond.

Author contributions

Conceptualization: JQ; data curation: HF, AS, and JQ; formal analysis: HF and AS; funding acquisition: JQ; investigation: HF, AS, and JQ; methodology: AS and JQ; project administration: JQ; resources: JQ; supervision: JQ; validation: HF; visualization: HF, AS, and JQ; writing–original draft: JQ; and writing–review and editing: HF, AS, and JQ.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article have been included in the supplementary information (SI) and are further available upon request from the authors. Supplementary information: detailed experimental methods (synthesis and characterization), including UV-vis, electron microscopy and catalysis data. See DOI: https://doi.org/10.1039/d5ta08597g.

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