Fewer, but better: on the benefits of surfactant-free colloidal syntheses of nanomaterials

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Abstract

Colloidal syntheses are common bottom-up synthetic approaches to obtain various nanomaterials, e.g. gold nanoparticles, where a precursor, e.g. $HAuCl_4$, is reduced in presence of reducing agents in a solvent. It is often claimed, and almost dogmatically believed, that stabilizers, capping agents, ligands, surfactants or other additives, *must* be added to ensure the stability of the colloids. Although there is almost a systematic use of such chemicals in the literature, a range of surfactant-free, or additive-free, colloidal syntheses have been reported. In those syntheses, the solvent plays the role of source of reducing agents and/or stabilizers. Recently, the use of alkaline solutions of low viscosity mono-alcohols, such as ethanol, has been shown to lead to stable surfactant-free colloids for various metal nanoparticles. Here, with the example of gold nanoparticles obtained at room temperature, it is shown that adding commonly reported stabilizers, such as trisodium citrate, PVP, SDS, poly(NIPAM), CTAB, or chemicals such as hydroquinone, actually does not lead to any advantages compared to the surfactant-free colloidal synthesis performed in alkaline mixture of water and 20 v.% ethanol. The results stress the potential of surfactant-free approaches compared to more conventional surfactant- and additives- assisted strategies to develop greener research studies and syntheses.

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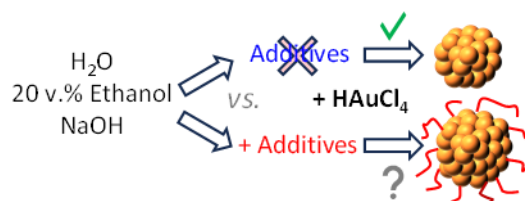
1. Introduction

Nanomaterials (NMs) with dimensions less than 100 nm are highly investigated and on high demand due to their unique properties relevant for applications in catalysis, e.g. as catalyst or catalyst support,[1-3] water/air treatment,[4,5] optics[6] or medicine.[7] The controlled synthesis of NMs is a necessary first step to study and exploits their full potential.[1,2] While a range of synthetic methods have been reported, colloidal wet-chemistry-based syntheses are one of the most popular strategy in academia.[2,8,9] If the benefits of colloidal syntheses to obtain various NMs, with various compositions, shapes or structures do not need to be demonstrated, *how* researchers obtain such materials remain to a large extent based on trials-and-errors.[2]

The largely preferred trials-and-errors approach results from: (i) the inherent relative diversity and complexity of colloidal syntheses, sensitive to multiple parameters, typically requiring several chemicals, and the fact that reactions can be carried out in different reactors and/or the synthesis induced in different ways;[10,11] (ii) a relatively poor understanding of the actual detailed formation mechanism of most NMs,[12,13] as a consequence of this relative complexity; and (iii) the fact that the field is driven by line of thoughts and concepts that are certainly convenient guidelines to develop NMs but not always descriptive enough. The present work (a) challenges the very strong belief that *additives are needed* to obtain stable colloidal NPs,[14,15] and (b) shows that *additives* can actually play a detrimental role in NP controlled syntheses.

In a typical colloidal synthesis, for instance for metallic nanoparticles (NPs), one or few metal atoms in an oxidized state in a molecular precursor are reduced in a solvent to a metallic state.[11] This is typically achieved in presence of reducing agents.[16] Once the first metal-metal bonds are formed, the NP will grow.[17,18] The growth will stop if no more precursor is provided and/or if stabilizing agents are used to control or prevent the growth. The stabilizing agents are often used from the beginning of the reaction and it is frequently stated that these additives *must* be used, to obtain stable, size controlled colloids.[9,14] The need for stabilizers is certainly true: the NPs need to somehow be stabilized by electrostatic and/or steric interactions, otherwise the NPs will keep growing to larger or even bulk materials.[14] The need for additives, i.e. adding a chemical for the sole purpose of stabilizing the NPs, is more debatable. What type of stabilizer can and should be selected, at which concentrations it should be used, etc., is very challenging to predict. This in part due to the fact that those additives can play the multiple roles of stabilizers but also reducing agents and/or pH buffer.[19] A typical example is the complex role of citrate in the well-established, yet still heavily studied, Borowskaja-Turkevich-Frens synthesis.[17,20] Although that synthesis requires only water, citrate and a gold precursor, more than 70 years of study have shown that a full control over the synthesis of the Au NPs is far from trivial. This complexity can be attributed to the complex chemistry of citrate and $HAuCl_4$ that can lead to a range of scenarios, and the fact that the NP size range obtained depends also crucially on how the synthesis is performed, for example on the type of reactors used.[21]

It is expected that a detailed framework, explaining what key factors drive the formation of NMs, could help by-passing some of the above-mentioned experimental challenges.[12,17] Arguably, the frameworks available to date to rationalize the formation of NMs are useful guides. However, as our understanding of NM formation progresses, it becomes clear that models such as the La Mer theory,[22] the classical nucleation theory,[18] or the Finke-Watzky kinetics model,[23] all have their limits. One reason is that these frameworks are necessarily first developed on model systems. Over the years, we came to challenge those model systems,[13] in particular when it comes to the role of additives in colloidal syntheses. While additives have often been considered important factors for post-synthesis stabilization, recent frameworks in the colloidal synthesis of NMs increasingly stress the inherent role of ligands / capping agents / surfactants / functionalizing agents *during the formation* of NMs.[24-26] This makes sense since these species are almost always present at the beginning of the synthesis, i.e. even before the reaction proceeds. The presence of these additives *from the beginning* is likely to have several effects given that different concentrations lead to different NP sizes (e.g. it is typically stated that the resulting size of Au NPs depend on the amount of citrate in citrate-based syntheses).[17,26] These species might also interact with the precursor and potentially change its redox properties, and therefore alter the formation pathway. However, to date, there are only few examples of cases where the additives can be omitted and yet stable NPs can be obtained, i.e. there are only few examples where study could be performed with a suitable control *without* additives.

In this regard, the development of *surfactant-free,* or *additive-free* colloidal NPs is an interesting new tool.[14] Surfactant-free NPs can be challenging to define and we here adopt a definition focusing on the synthesis process, that considers that a synthesis is surfactant-free if no chemicals with a molar mass more than 100 g mol^{-1} is used in the synthesis (excluding the precursor for metal NPs). This definition also excludes the addition of any support often used in a common *one-pot* synthesis.[27] While no additives are used, the resulting colloidal dispersions are stable for months or years without significant agglomeration of the NPs. Only a handful of methods lead to surfactant-free metal NPs including laser ablation, plasma processing, DMF-based syntheses, polyol- and mono-alcohol mediated syntheses, reviewed elsewhere.[14] The NPs are stabilized by electrostatic phenomena and/or interactions with the solvents, and/or interaction with small molecules such as CO, and/or viscosity of the solvents. In particular, it is worth stressing that a range of small size (typically 2-20 nm) and stable metallic NPs, including Pt,[8] Ir,[28] Ru,[8] Os,[29] Pd,[15] or Au[15] can be prepared in alkaline water-ethanol mixtures, at relatively low temperature, without the need for any additives. Those syntheses were mainly developed to obtain relatively *clean* NMs relevant for catalysis, obtained in low boiling point solvents, which facilitates their processing, for instance to develop heterogeneous catalysts.[30,31]
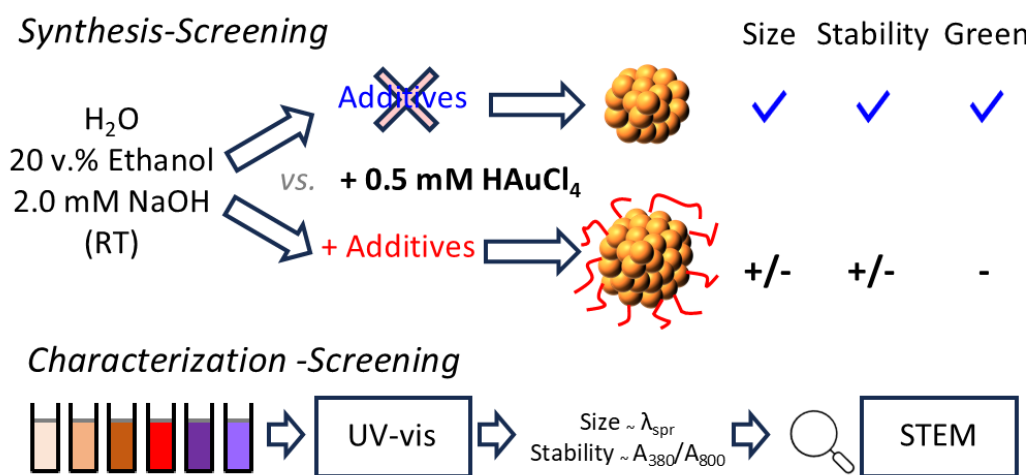
Figure 1. General concept and methodology to exploit the unique benefits of surfactant-free colloidal syntheses and to investigate the influence of additives on Au NP synthesis.

Here, we demonstrate that surfactant-free syntheses also offer new avenues to understand NP formation. We take advantage of the fact that stable colloidal NPs are obtained without the need for additives to assess the impact of adding several additives commonly used, as illustrated in **Figure 1** and **Table 1**. As a case study, we focus on a recently reported room temperature surfactant-free colloidal synthesis of Au NPs performed in alkaline 20 v.% ethanol in water mixtures using $HAuCl_4$ as precursor.[15] The results challenge the strong belief that additives are needed to obtain small size, size-controlled and stable NPs, by showing that in most cases the additives actually play a detrimental role.

2. Materials and methods

An overview of the parameters investigated in this study and the general strategy is proposed in **Figure 1** and further details are provided in **Supporting Information** (SI).

2.1 Chemicals

All chemicals were used as received: $HAuCl_4 \cdot 3H_2O$ (BLD Pharmatech, 99%,); high purity water (mQ, Milli-Q, resistivity ≥18.2 MΩ·cm); ethanol absolute (VWR, ≥99.8% Ph. Eur., USP); NaOH (Sigma Aldrich, reagent grade, ≥98%, pellets); trisodium citrate·$2H_2O$ (NaCt, Sigma Aldrich, BioUltra); polyvinylpyrrolidone (PVP, Sigma Aldrich, average mol wt 10 000); sodium dodecyl sulfate (SDS, Sigma Aldrich, ReagentPlus®, ≥98.5%); poly(N-isopropylacrylamide) (poly(NIPAM), Sigma Aldrich, average M_n 5500 (T), amine terminated); hexadecyltrimethylammonium bromide (CTAB, Sigma Aldrich, BioXtra, ≥99%); hydroquinone (HQ, VWR, ≥99%, GPR RECTAPUR®); HCl (puriss. ACS reagent,

reag. ISO, reag. Ph. Eur. fuming, ≥37%, Sigma Aldrich); HNO_3 (puriss ≥ 65%, Sigma Aldrich).

2.2 Au NP synthesis

Surfactant-free synthesis. The surfactant-free Au NP synthesis followed the general recipe reported in detail in previous work.[15,32] In summary, mQ,[32] NaOH (from a stock solution at 50 mM prepared in mQ and kept in Nalgene flask)[33] and ethanol[32] were mixed in a polystyrene (PS) disposable UV-vis cuvette (1 cm wide rectangular shape), de-dusted with compressed air and containing a magnetic bar (PTFE cylindrical stirrer bar, 8 x 3 mm, VWR) cleaned with *aqua regia* (4:1, v:v, HCl:HNO_3 – to be handled and disposed of following the regulation enforced in the work environment since this solution is highly acidic and corrosive).[32] The final content in v.% varied between 0-20 v.% (although without reducing agent the reaction does not proceeds), the concentration of NaOH was 0.8 mM or 2 mM, as indicated. To the mixture, $HAuCl_4$ (from a 50 mM stock in mQ, prepared in a glass container and stored in the fridge) was added under stirring at room temperature and under controlled light environment (Photo box, Puluz LED portable Photo Studio, PU5060EU, 60 cm x 60 cm x 60 cm, 60 W).[32,34] The final concentration of $HAuCl_4$ was 0.2 or 0.5 mM, as indicated leading to a NaOH/Au molar ratio of 4. The final volume of solution was 2 mL, before taking into account volume contraction. The UV-vis cuvette were then closed with dedicated caps.[32] The synthesis was left to proceed for 2 hours under stirring, then the samples were sealed with Parafilm, left overnight at ambient room temperature and light before being stored at room temperature in a drawer.

Table 1. Table of the additives used and overview of the experimental conditions investigated.

Additives	Ethanol v.%	$HAuCl_4$ mM	Additive / Au molar ratio
NaCt	0, 5, 10, 20	0.2, 0.5	0, 5, 10, 15
PVP	20	0.2, 0.5	0, 2, 5, 10, 15, 20
SDS	20	0.2, 0.5	0, 1, 2, 5, 10, 15
poly(NIPAM)	20	0.2, 0.5	0, 1, 2, 5, 10, 15
CTAB	20	0.2, 0.5	0, 1, 2, 5, 10, 15
HQ	0, 5, 10, 20	0.2, 0.5	0, 1, 2, 5, 10, 15

Synthesis with additives. To test the influence of various additives for which an overview is given in **Table 1**, the previous conditions were used together with stock solutions of NaCt (at 50 mM), PVP (at 50 mM), SDS (at 50 mM), poly(NIPAM) (at 50 mM), CTAB (at 10 mM) and HQ (at 50 mM), all in mQ, prepared in glassware. The chemicals were mixed in the ratios detailed in **Table 1** or discussed below. The $HAuCl_4$ solution was always added last, unless otherwise specified.

2.3 Characterization

UV-vis. UV-vis spectra of the samples were taken 24 hours after the synthesis (i.e. 24 hours after the addition of the last chemical), unless otherwise specified, with a Thermo Scientific Genesys 10s UV-VIS spectrophotometer in the wavelength range 290-800 nm on the as-prepared colloidal dispersions in the UV-vis cuvettes. A water-ethanol solution was used as baseline with equivalent ethanol content to that of the sample, since none of the other used chemicals had significant absorption in the range of the measurement, apart from alkaline solutions of HQ (as detailed later). A set of parameters detailed in previous report and emphasized in **Table S1** in **SI** were retrieved for characterization from the spectra. In particular the position of the surface plasmon resonance (spr) of the Au NPs (λ_{spr}) gives indication on the size of the Au NPs (where lower λ_{spr} values correspond to smaller NPs)[35] and the A_{380}/A_{800} value gives an indication of the stability of the colloids (higher A_{380}/A_{800} values correspond to more stable dispersions).[36]

Scanning Transmission Electron Microscopy (STEM). STEM micrographs were taken on an FEI Talos F200X. The microscope was operated at 200 kV and the apparatus is equipped with High-Angle Annular Dark-Field detector. The colloidal dispersion prepared by the above-described synthesis were directly dropped on copper TEM girds (300 mesh. Sigma-Aldrich). After solvent evaporation, the measurements were performed on the dried NPs. Size distributions were acquired with ImageJ from at least a 100 NPs.

2.4 Methodology and Green Chemistry

One benefit of the developed surfactant-free colloidal syntheses performed at room temperature in ethanol-water mixture is to allow a relatively high throughput without requiring advanced equipment. This makes this synthetic approach ideal for screening studies as the one proposed here on the influence of additives, as illustrated in **Figure 1**. While it is common to perform several characterization techniques on NMs,[37,38] performing all the techniques on all the samples will be too much time- and resource-consuming. Due to their plasmonic properties, UV-vis allows a rather comprehensive characterization of the Au NPs by a relatively high throughput and cost-effective technique.[39-41] Only selected samples were characterized by more advanced electron microscopy technique. It is worth pointing that the plasmon properties of Au NPs depend on their size and/or shape but also their surrounding environment. Therefore, *stricto sensu,* the different UV-vis spectra and the related retrieved value might not be comparable for different additives used and/or different concentrations of additives used. However, in our experimental experience across the comparison of now over 1000 samples, the comparison still leads to meaningful results and guidelines.[15,34,42]

It is worth nothing that the proposed approach also complies with the (re-)emerging principles to adopt more *sustainable* practices in the laboratory.[43] The preference for a room temperature process to perform the screening detailed below overall minimizes energy consumption. The synthesis requires only relatively benign chemicals.[44] Also, the use of small volumes minimizes waste, the use of disposable cuvettes (although they generate plastic waste) minimizes the need to use and dispose of hazardous *aqua regia,*[9] but also facilitates the labelling and storage of the samples.

3. Results and Discussion

The present study aims to evaluate the potential benefits of adding several commonly used additives to an otherwise surfactant-free synthesis of Au NPs. It is often reported that several additives can help to achieve size control and/or higher stability. In the context of this study, it is considered that obtaining small size and stable colloidal NPs is more challenging. Therefore, a positive result is characterized by a UV-vis spectra with a low λ_{spr} value[35] and a narrow peak[45] with high A_{380}/A_{800} values.[36] The focus is on using the additives from the beginning of the synthesis but results for the addition 24 hours after the beginning of the synthesis can be found in **Figure 11**, detailed later.

3.1 Surfactant-free synthesis

It is established that without the need for surfactant, the mixture of mQ, NaOH, ethanol and $HAuCl_4$ in the right proportions leads to Au NPs ca. 10 nm in size that are stable for months and even years.[15,32] The HAuCl45 is the source of Au atoms, water is the solvent, and the alkaline conditions lead to the formation of alkoxides that will play the role of reducing agents.[46] An optimal synthesis leading to small size ca. 10 nm NPs is best performed using 0.5 mM $HAuCl_4$, ca. 2 mM NaOH and 20 v.% ethanol. Size control can be achieved by tuning in particular the NaOH/Au molar ratio and/or the nature of the mono-alcohol and alcohol content, as detailed elsewhere.[15] Although the synthesis can be performed in relatively small volumes, it also scales up well to e.g. 1 L, as illustrated in **Figure 2**. The NPs kept a relatively small size (12.3 ± 5.2 nm) even after 3 years of storage. Since the literature stresses the *need* for surfactants, we here study in details the impact that adding common reported stabilizers has on the present surfactant-free colloidal synthesis of Au NPs.
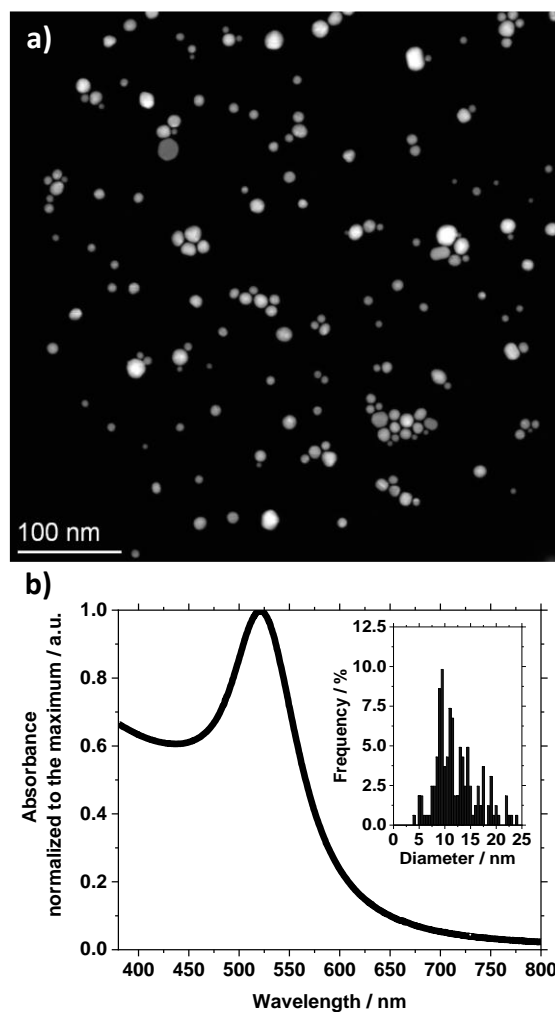
Figure 2. Examples of surfactant-free colloidal Au NP prepared using 20 v.% ethanol, 3.8 mM NaOH, 0.5 mM HAuCl$_4$ in a 1 L batch in a Pyrex container prepared and reported in [15] characterized after 3 years of storage in a fridge. (a) STEM micrograph and (b) UV-vis data. The inset in (b) is the corresponding size distribution.

3.2 Effect of NaCt

We first investigated the effect of adding NaCt to the surfactant-free colloidal synthesis. NaCt is widely used in colloidal syntheses of Au NPs, and often with a NaCt/Au molar ratios around 5-10.[9,17] The ratio of citrate to gold is reported to have a strong influence on the NP size, in part because it conditions the pH that plays an important role in the synthesis. In agreement with our preliminary results,[15] **Figure 3** confirms an influence of the NaCt/Au molar ratio on the size of the NPs. As the NaCt/Au molar ratio increases, the Au NPs get larger in average size and in size distribution with sizes: 14.2 ± 5.1, 12.8 ± 5.1 6.1 and 38.8 ± 21.7 nm for NaOH/Au molar ratio of 0 (surfactant-free), 5 and 10, respectively (see size distributions in **Figure S1**). This agrees with the corresponding UV-vis spectra showing higher λ_{spr} values, a broadening of the spr peak, a larger tail with higher intensities at higher wavelengths (that leads to lower A$_{380}$/A$_{800}$ values) indicative or lower stability. The sample prepared with a NaOH/Au molar ratio of 15 did not lead to

stable colloids as indicated by the very low intensity of the UV-vis spectrum in **Figure 3d**, and therefore was not characterized further. A similar trend is observed based on UV-vis for 0.2 mM HAuCl$_4$ used, see **Figure S2**.
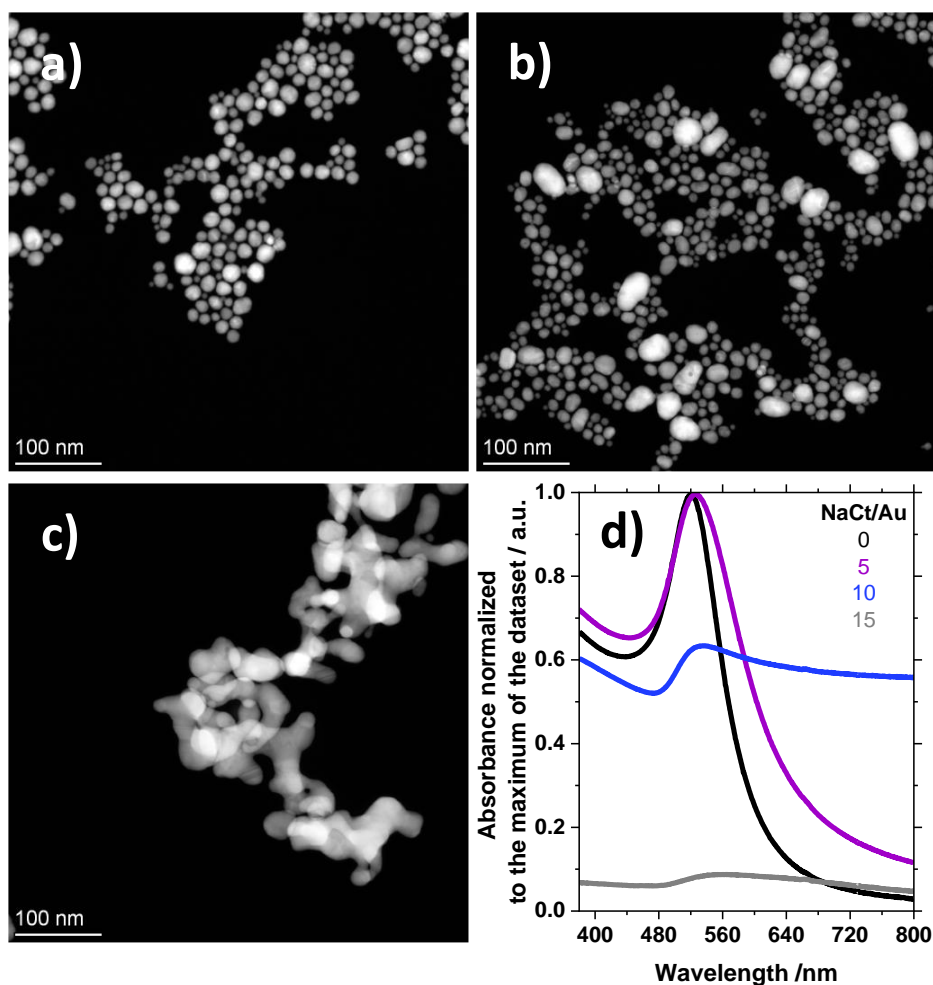

Figure 3. (a-c) STEM micrographs of Au NPs obtained (a) without NaCt, (b-c) with a NaCt/Au molar ratios of (b) 5 and (c) 10. (d) UV-vis spectra of the corresponding samples, as indicated. The results were obtained using 0.5 mM HAuCl$_4$ and 2 mM NaOH. No STEM micrographs were recorded for the NaOH/Au molar ratio of 15 due to the low stability of that sample.

These results show that there is no need for NaCt to control the size of the AuNPs towards smaller sizes, nor to improve the stability of the colloids. A reasonable explanation in the present case to explain the results is that NaCt and ethanol can both play the role of source of reducing agents.[15,16] It can then be hypothesized that the excess of reducing agent can lead to a too strong reduction leading to unstable colloids, given that the formation of colloids often results in a balance between the kinetics of formation and adequate stabilization.[15,16]

To investigate further this hypothesis, it is natural to try reducing the amount of ethanol when the amount of NaCt increases. It should however be kept in mind that ca. 20 v.% ethanol seems to be an optimal case for the surfactant-free version of this synthesis,[15,34] as illustrated in **Figure 4a**, where a well-defined spr is only observed at 20 v.% ethanol. **Figure 4** reports the UV-vis spectra recorded for different NaOH/Au molar ratios and ethanol contents, as indicated, where the whole dataset is normalized to the same maximum to help cross-panels comparison. Comparing in particular **Figure 4a** and **Figure 4d** that display the two extreme cases of no NaCt and a NaCt/Au molar ratio of 15, it is observed that as the NaCt/Au molar ratio increases, relatively more pronounced spr features are observed when the ethanol content tends to decrease. It is also confirmed that without ethanol and without NaCt, no NPs are formed (no signal in the UV-vis, **Figure 4a**).

These results tend to support the hypotheses that both ethanol and NaCt play the role of reducing agents and stress the benefits for surfactant-free synthesis for which the UV-vis data indicated the smaller and more stable Au NPs. The best defined plasmonic features indicative of small size spherical Au NPs are obtained without additives.
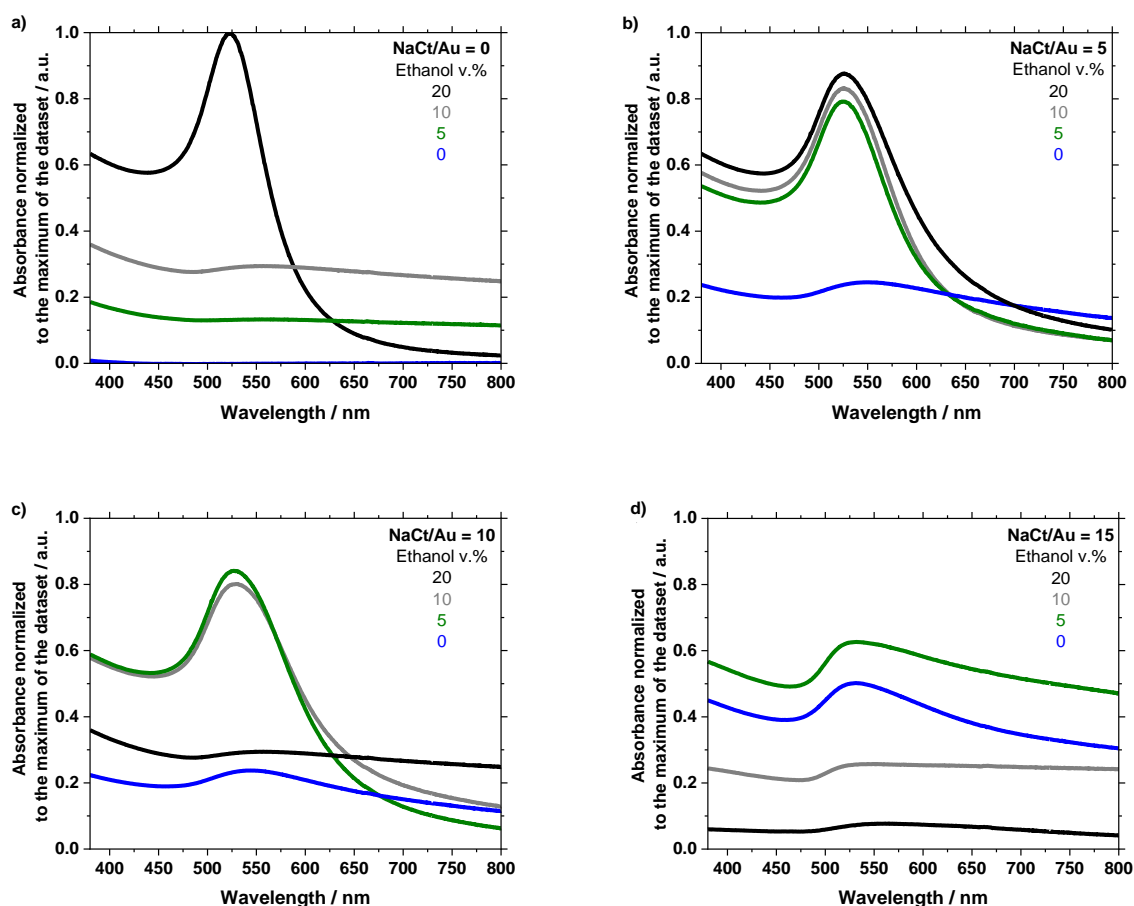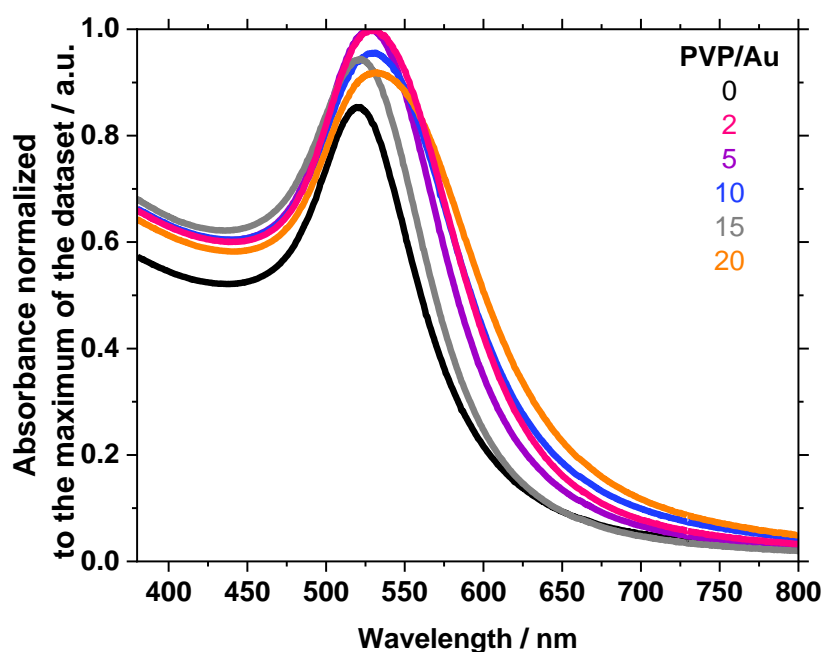

Figure 4. UV-vis spectra for Au NP dispersions obtained for different ethanol contents, as indicated, and different NaCt/Au molar ratios of (a) 0, (b) 5, (c) 10 and (d) 15. The all

dataset is normalized to the same maximum to facilitate cross-panels comparison. The $HAuCl_4$ concentration was 0.5 mM and the NaOH concentration was 2 mM.
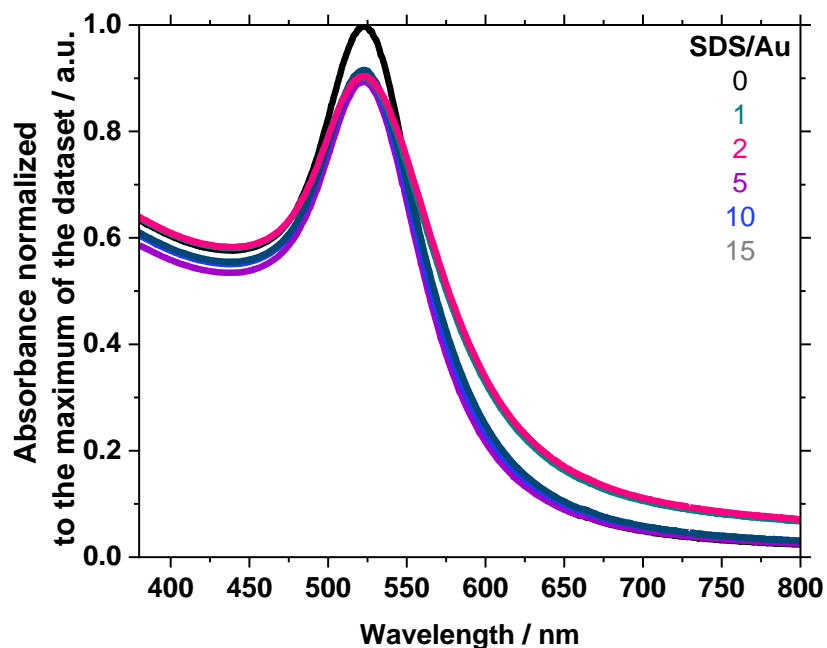
3.3 Effect of PVP

PVP is probably one of the most common additives to various NP syntheses.[47] PVP acts as stabilizer but can also play the role of reducing agent.[16] In the case of addition of PVP at different PVP/Au molar ratios, as reported in **Figure 5** and **Figure S3**, the UV-vis spectra show higher λ_{spr} values and a broader peak, indicative of larger NPs. The correlation between the amount of PVP used and the resulting UV-vis spectra is not as clear as in the case of NaCt (section 3.2). The results therefore suggest that there is no benefit to use PVP in the present ethanol-mediated synthesis.

Figure 5. UV-vis spectra for Au NP dispersions obtained for different PVP/Au molar ratios, as indicated, for 0.5 mM $HAuCl_4$, 2 mM NaOH and 20 v.% ethanol.

3.4 Effect of SDS

SDS is a common surfactant and detergent that does not only increase the stability of the NPs but can also be used to control the size and morphology of the NPs.[48] SDS was showed to be effective in forming faceted penta- and hexagonal NPs, due to its lamellar instead of a spherical micellar structure.[49] As indicated in **Figure 6** and **Figure S4**, the UV-vis peak show similar λ_{spr} values and peak broadness. Since SDS is not a strong reducing agent, the effect of adding SDS is less pronounced than for NaCt (section 3.2) and PVP (section 3.3). It is still concluded that there is no benefit to use SDS.

Figure 6. UV-vis spectra for Au NP dispersions obtained for different SDS/Au molar ratios, as indicated, for 0.5 mM HAuCl$_4$, 2 mM NaOH and 20 v.% ethanol.

3.5 Effect of poly(NIPAM)

Poly(NIPAM)) was reported to increase the stability of AuNPs.[50] The temperature sensitivity of poly(NIPAM) opens the door to thermally control surfactant adsorption on the surface of the NPs and develop temperature and salt sensors.[51] Based on the UV-vis spectra reported in **Figure 7** and **Figure S5**, given the broader spr features observed and/or low absorption intensity recorded, it is concluded that the use of poly(NIPAM) is not beneficial compare to the surfactant-free colloidal synthesis. This agrees with the fact that adding poly(NIPAM) after the reaction is completed also leads to less stable colloids, **Figure 11**.
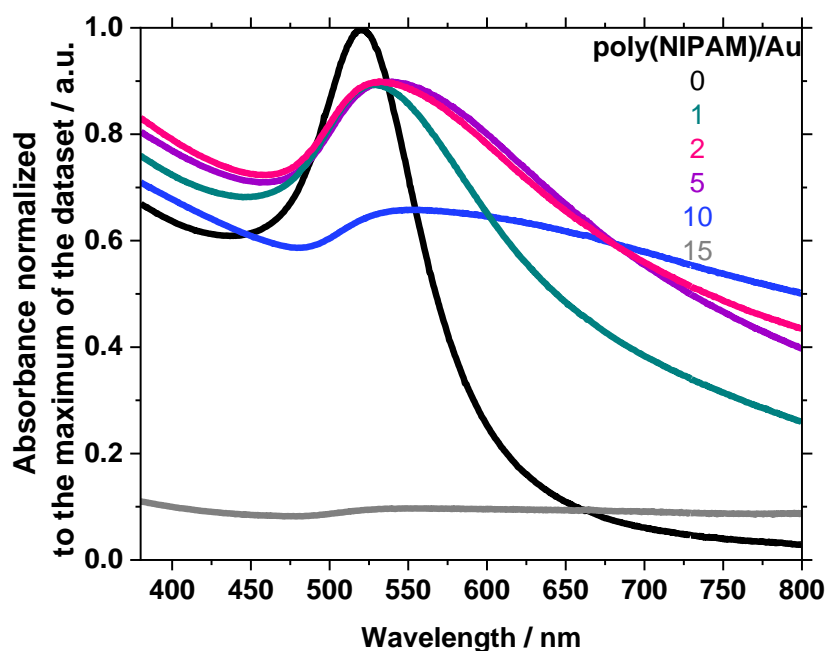
Figure 7. UV-vis spectra for Au NP dispersions obtained for different poly(NIPAM)/Au molar ratios, as indicated, for 0.5 mM $HAuCl_4$, 2 mM NaOH and 20 v.% ethanol.

3.6 Effect of CTAB

CTAB is a widely used chemical for Au NM syntheses,[9] e.g. for seed mediated syntheses.[52] CTAB is typically premixed with $HAuCl_4$ and stirred, to form micellar CTAB-Au complexes. The complexes exhibit yellow/orange/light red colors, which can be misinterpreted as NPs. CTAB has a higher affinity to attach to the <100> than the <111> crystal facets of Au, causing rapid elongation along the <110> axis, which yields rod-shaped NPs.[53] The results reported in **Figure 8** and **Figure S6** confirm that the use of CTAB does not bring any benefit in the case of the surfactant-free colloidal synthesis. This is in line with previous reports showing that CTAB can be detrimental to NP formation in some cases.[54] This is also in agreement with the fact that adding CTAB after the reaction is completed leads to less stable colloids, **Figure 11**.
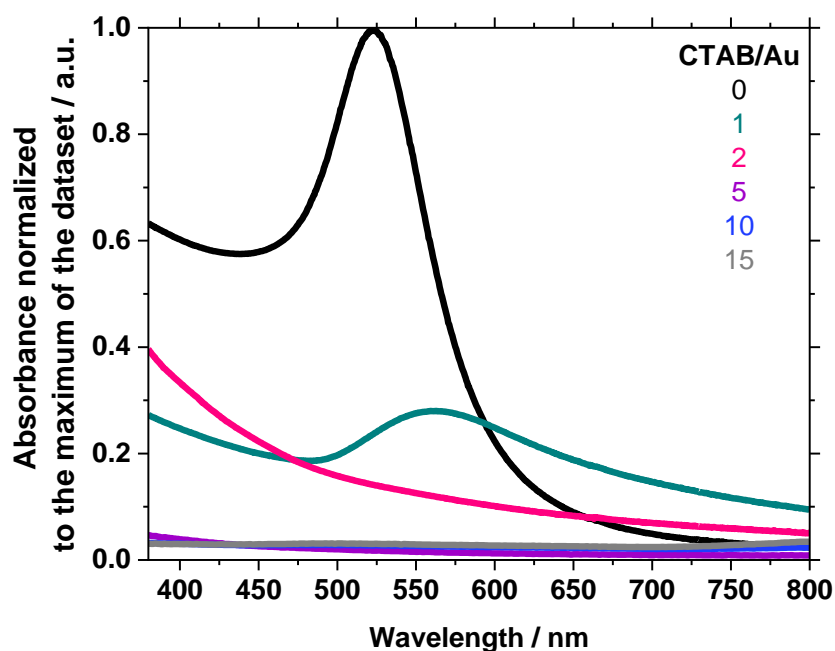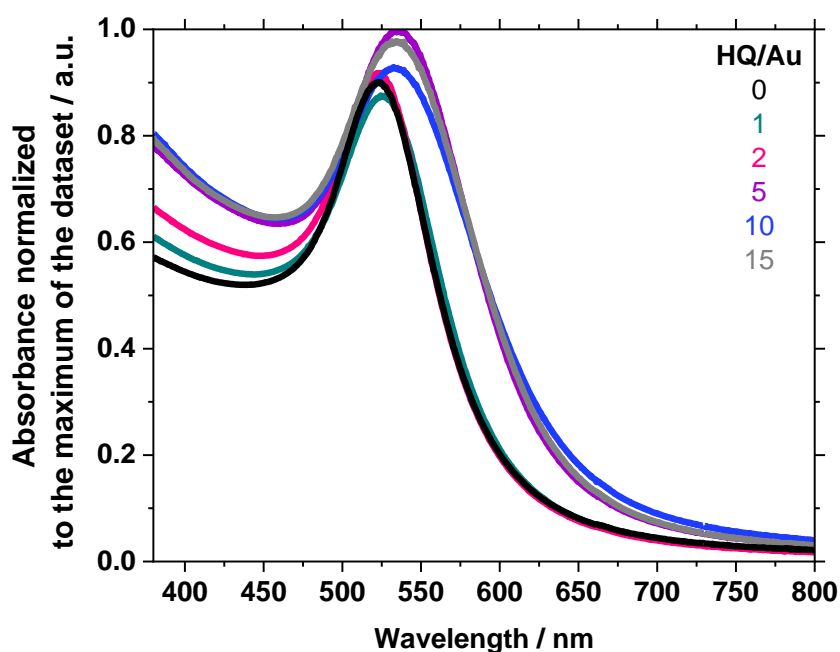
Figure 8. UV-vis spectra for Au NP dispersions obtained for different CTAB/Au molar ratios, as indicated, for 0.5 mM HAuCl$_4$, 2 mM NaOH and 20 v.% ethanol.

3.7 Effect of HQ

On a slightly different note, we also considered in this study the use of HQ that is a reducing agent in aqueous solution, similarly to mono-alcohols in the present surfactant-free synthesis.[16,55] It has been shown that raising the pH over 7 by addition of NaOH significantly enhances the reductive affinity of HQ. However, pH above 9 causes irreversible oxidation to benzoquinone, resulting in uncontrolled precipitation of gold. Further results show that HQ is ineffective as a reducing agent at pH 2, but over pH 4 rapid aggregation and precipitation of NPs occur. The expected stochiometric molar ratio fort the reduction of Au^{III} by HQ is HQ/Au^{III} equal to 1.5, as 2 electrons are needed for HQ to benzoquinone oxidation. Excess HQ concentration was shown to repress NP formation. NPs with a mean diameter of 20.5 nm was produced with this method and Sirajuddin et al. suggested that the secondary product, benzoquinone is an effective capping agent for the Au NPs.[55]

When HQ was used the reactions proceeded very fast. A color change is observed almost immediately after adding the HAuCl$_4$. As opposed to the several hours needed to observe a color change in the case of the surfactant-free synthesis and the several minutes required when other additives were used. This is attributed to the strong reducing ability of HQ. **Figure 9** and **Figure S7** illustrate that there is also no benefits to use HQ: The UV-vis spectra of surfactant-free colloidal NP indicate smaller and as or more stable dispersions. Note that the higher absorption at lower wavelengths (e.g. around 400 nm)

might indicate a higher NP yield but is more likely resulting from the absorbance of species formed under alkaline conditions from HQ, see **Figure S8**. HQ absorbs at low wavelengths, and features in the range 400-500 nm appears under alkaline conditions. Furthermore, in **Figure 9**, the absorption increases as the HQ amount increases, although the stoichiometric ratio for which a full conversion of the Au^{III} to Au^0 should be reach around values of HQ/Au molar ratios around 1-2. Finally, the addition of HQ after the reaction is completed does not lead to a different spectrum, suggesting that an optimal yield is achieved in the surfactant-free synthesis (no further reduction after addition of a reducing agent), **Figure S11**.

Figure 9. UV-vis spectra for Au NP dispersions obtained for different HQ/Au molar ratios, as indicated, for 0.5 mM HAuCl₄, 2 mM NaOH and 20 v.% ethanol.

In **Figure 10**, it is illustrated, in a similar case to NaCt (section 3.2), that decreasing the amount of ethanol while the amount of HQ increases (to balance the total amount of species playing the source of reducing agents) does not lead to any benefits compared to performing the surfactant-free synthesis that still leads to the colloidal dispersions with the lower λ_{spr} values and narrower spr peak.
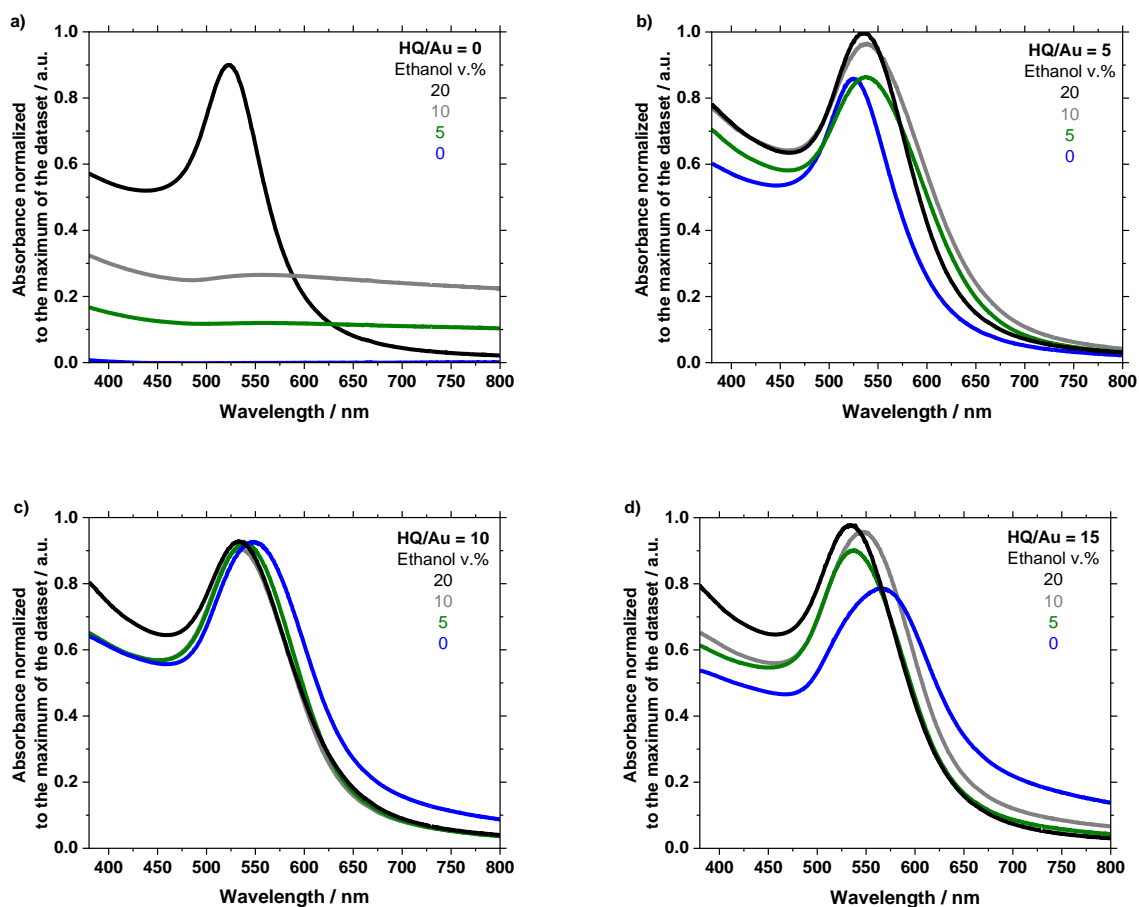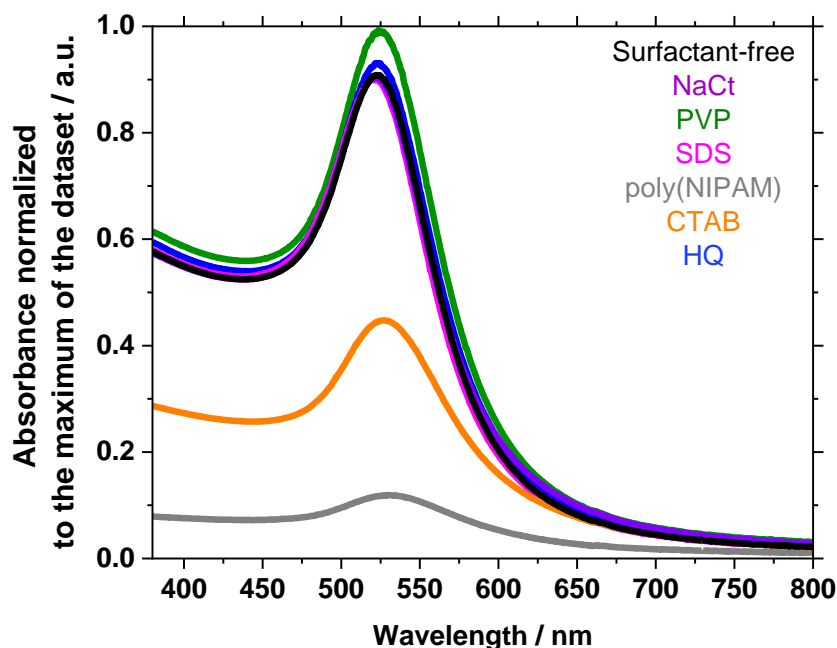
Figure 10. UV-vis spectra for Au NP dispersions obtained for different ethanol contents, as indicated, and different HQ/Au molar ratios of (a) 0, (b) 5, (c) 10 and (d) 15. The whole dataset is normalized to the same maximum to facilitate cross-panels comparison. The $HAuCl_4$ concentration was 0.5 mM and the NaOH concentration was 2 mM. The panel (a) is the same as panel (a) in Figure 4 with a different normalization.

3.8 Time delayed addition of the additives

To assess the effect of adding the additives on already formed Au NPs, the additions of the additives was performed 24 hours after the water, base, ethanol and $HAuCl_4$ were mixed. The results are reported in **Figure 11**. The spectrum for the surfactant-free synthesis were not much changed by the addition of NaCt, PVP, SDS or HQ whereas the NPs became unstable upon adding poly(NIPAM) or CTAB as indicated by the lower absorbance recorded for these two additives. Adding the additives did not have a strong effect on the λ_{spr} values. The slightly higher value of absorbance for PVP is attributed to slightly different $HAuCl_4$ concentration is that particular sample and is related to experiment errors and/or an effect of PVP on the media surrounding the NP which can influence the UV-vis spectra.

Figure 11. UV-vis spectra for Au NP dispersions obtained for different additives added 24 hours after the reaction was initiated, and left another 24 hours after UV-vis measurement, as indicated, for an Additive/Au molar ratio of 15, for 0.5 mM $HAuCl_4$, 2 mM NaOH and 20 v.% ethanol.

3.9 Discussion

A summary of the results obtained is plotted in **Figure 12** where samples with desirable low λ_{spr} values and high A_{380}/A_{800} values are easily identified. From this plot, it becomes clear that adding species with redox properties and/or with the ability to stabilize the NP does not lead to any obvious benefit to the controlled synthesis of Au NPs, compared to the surfactant-free version. The data plot 'PVP 15' might indicate an improvement but in line with the other data obtained using PVP this is likely an outsider and the benefit to use PVP is minimal compared to the detrimental effect in application such as catalysis documented elsewhere.[56] Note that in this plot the samples obtained with HQ are excluded due to the unsuitability of the A_{380}/A_{800} metric to describe stability when HQ is used (see section 3.7). An alternative plot using the A_{650}/A_{spr} metric, where lower values indicate more stable NPs, confirms that using HQ does not lead to any obvious benefits to the synthesis, **Figure S9**.
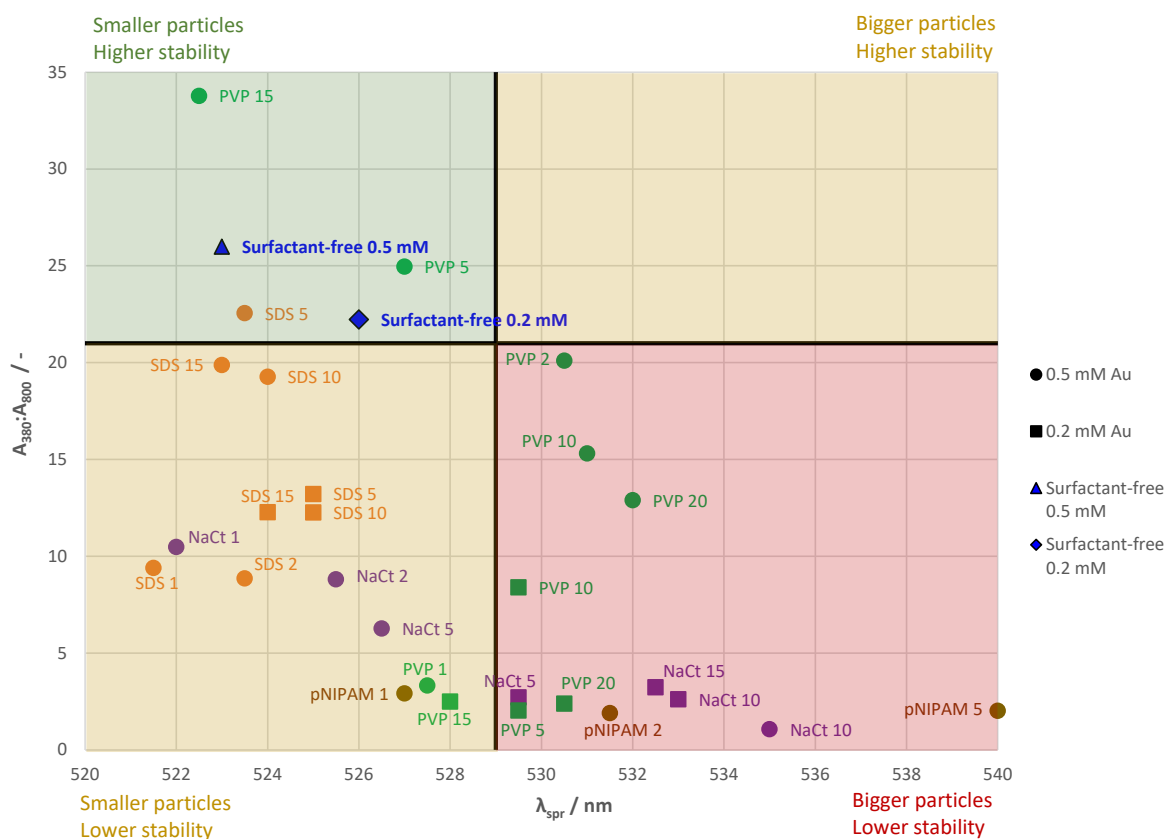
Figure 12. Overview of the size-stability (λ_{spr} – A_{380}/A_{800}) parameter space retrieved from UV-vis characterization for Au NPs obtained using different additives in different amount, as indicated. Note that samples prepared with all ratios of CTAB and ratios of 10 and 15 of poly(NIPAM) (abbreviated pNIPAM here) are not visible. This is due to the fact that those experiments resulted in no NP formation, or NPs with significantly lower stability. In all cases the ethanol content was 20 v.% and the NaOH/Au ratio was 4. Samples using HQ were omitted since the A_{380}/A_{800} metric is not suitable for use, as discussed in the text. The concentration of $HAuCl_4$ was 0.2 or 0.5 mM, as indicated. The nature of the additives is reported with abbreviation and color code as indicated and the number associated with each data point corresponds to the Additive/Au molar ratio.

In particular, the fact that most species can play the role of reducing agents does not combine positively with the already demonstrated ability of alkaline water-ethanol mixture to lead to the $HAuCl_4$ reduction. The use of stabilizers is also not a necessity given the long shelf life of the Au NPs obtained without surfactants, **Figure 2**. Lower concentrations of surfactant seemed to result in smaller size, size distribution and higher stability of the NPs. This could be caused by the reversed effect of surfactants at higher concentration, where too many surfactant molecules aggregate and form micelles and/or favor the agglomeration of the Au NPs by developing additive-additive interactions that bring the Au NP surfaces close to each other. Adding surfactants after the synthesis is completed did not lead to any benefits, **Figure 11**, or even lead to less stable dispersions in the case of poly(NIPAM) and CTAB.

It is worth pointing out that the outcome of the synthesis adding the additives after 24 hours is less pronounced based on UV-vis spectra that when the additives is present from the beginning of the synthesis. For instance, using additives on pre-formed Au NPs does not seem to influence much the Au NPs size and/or agglomeration (except for poly(NIPAM) and CTAB for the stability). This result stress the influence of additives *during* Au NP formation.

Certainly, the different additives considered here have different chemical properties and will interact with $HAuCl_4$ and/or the Au NP surface in different ways. Certainly the synthesis could be optimized in terms of ethanol content and based concentration, for a given additive, to potentially lead to more stable and more size controlled NPs. However, the overview proposed here clearly establishes that several common additives are not required and can actually have detrimental effects on size control and stability compared to the surfactant-free synthesis.

It can be stressed that the use of multiple chemicals, unless they really bring a benefit to the controlled synthesis, come with several disadvantages. Most surfactants derive from fossil fuels,[57] the removal of surfactants can be challenging,[58] impurities can have a strong effects on NM synthesis,[59,60] and the more chemicals used, the more likely impurities are introduced, and the often multiple roles of additives as (source of) reducing agent(s) and stabilizers[17] can complicate their rational selection. To develop greener syntheses of NMs, the use of few and benign chemicals should be a preferred option.[61,62] In this sense, avoiding the use of toxic chemicals, such as CTAB or HQ, is a promising feature of surfactant-free colloidal syntheses. Finally, fewer and safer chemicals open unique avenues for large scale processes potentially more cost-efficient.

Certainly, ligands and other additives can bring positive features to control size, shape structures and ultimately properties.[63,64] The present work does not aim to question this rewarding strategy. Rather, the results presented show that additives are not always needed to obtain small size and stable Au NPs. While we provide only a screening of some common additives, the simplicity of the approach reported call to investigate other additives and it is anticipated that beyond their proven benefits of catalysis, surfactant-free syntheses have the potential to be new platform to study and guide the development or *greener* and more comprehensive syntheses of NMs.

4. Conclusion

In contrast to a popular belief, no surfactants are required to prepare at room temperature stable Au NPs obtained by adding $HAuCl_4$ to an alkaline (NaOH) 20 v.% ethanol in water mixture. The surfactant-free colloidal NPs are actually stable for years. Based on the plasmonic properties of the Au NPs when it comes to NP size and stability, it is here shown that the consequence of using 6 common additives reported to *improve* the synthesis actually leads to a poorer control over the NP properties.

The results show the potential of surfactant-free colloidal syntheses in alkaline mixtures of mono-alcohol and water as a suitable model system for new understanding of the key factors governing NP formation. Indeed, the fact that the synthesis can be performed at room-temperature allows a relatively high throughput that bears the potential to be exploited further for larger parametric screenings. It certainly remains challenging to explain why the addition of the selected additives lead to relatively worst results in light of the criteria selected here for the optimization the synthesis. Nevertheless, the results illustrate the promising features that the proposed model system has to offer: a simple, safe and relatively high throughput synthesis, relevant to screen and identify promising additives to select for future more in-depth studies.

A last benefit of not requiring surfactants is to develop *greener* syntheses of NMs, safer by requiring less (hazardous) chemicals and more resource-efficient, and therefore cost-efficient. For instance, the approach proposed minimizes the risk of introducing impurities detrimental to the NP properties by reducing the number of chemicals.[60] Ultimately, it is expected that the approach proposed will enable to identify the *minimal* amount of additives to achieve a given outcome such as a desired size or even shape control.

5. References

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