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Surfactant-free gold nanoparticles synthesized in alkaline water–ethanol mixtures: leveraging lower grade chemicals for size control of active nanocatalysts†

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Low(er) purity chemicals are often detrimental for nanomaterial synthesis. Here, lower grade chemicals, e.g. lower grade water, are used to achieve size control over surfactant-free gold nanoparticles simply obtained at room temperature in alkaline ethanol–water mixtures. The nanoparticles are active catalysts, e.g. for water treatment with the example of the reduction of 4-nitrophenol. The simple strategy reported to obtain size-controlled gold nanoparticles opens new door for the holistic development of sustainable nanotechnologies.

Introduction

Nanomaterials and nanoparticles (NPs) are promising materials with outstanding size-dependent properties relevant for catalysis, energy conversion, water/air treatment, sensing, optics, medicine, and many more.^{1–4} The full exploitation of the unique properties of NPs relies on their careful preparation, processing and combination with other (nano)materials.^{5,6} The holistic development of more sustainable nanotechnologies calls for the development of more sustainable and more affordable preparation methods of nanomaterials.^{7,8} Unfortunately, the development of alternative and more sustainable preparation methods of nanomaterials is far from trivial. Indeed, the formation and production of NPs, and therefore the resulting properties of the NPs, can strongly depend on multiple parameters such as the nature of the chemicals and/or processes used,⁹ but also the purity of the related chemicals and solvents.^{10,11}

In the quest to develop more sustainable and green technologies,⁷ using commercially available solvents¹² or relatively

Sustainability spotlight

Nanotechnologies can address several of the UN's Sustainable Development Goals (SDGs), provided green synthesis methods of nanomaterials are developed. In contrast to a widespread preference for high purity and expensive chemicals, we show the benefits of using lower purity chemicals to develop more sustainable syntheses of nanomaterials. As an example, gold nanoparticles with a relatively fine size control are simply obtained at room temperature in water–ethanol mixtures without surfactants under only slightly alkaline conditions. The nanomaterials are relevant nanocatalysts for water treatment. The research aligns with UN SDGs: industry, innovation and infrastructure (SDG 9), clean water and sanitation (6). The technology is also ultimately relevant for affordable and clean energy (SDG 7) and the concept for education purposes (SDG 4).

low grade and lower purity solvents and chemicals,¹³ are attractive sustainable options, for instance, using by-products of waste-generating technologies.¹⁴ It is worth stressing that these lower grade chemicals are also often cheaper and therefore more likely to be relevant for scale up. Water in particular is a to-be-preferred solvent,¹⁵ although it is known that the purity of water can strongly impact the outcome of NP syntheses.¹⁰ An example is the synthesis of gold (Au) nanoparticles (NPs), where high purity water is highly recommended.^{10,16} The need for high purity water is even more important in so-called surfactant-free (SF) colloidal syntheses, defined elsewhere,¹⁷ where electrostatic interactions play a key role in the NP stabilization.^{4,13,17}

In particular, recently reported SF syntheses of precious metal NPs performed in alkaline water–ethanol mixtures with high water contents (e.g. 80 v% water) present the benefits: (i) to require low energy (low temperature processes);^{18,19} (ii) to require few and benign chemicals, e.g. no need for fossil-fuels-derived surfactants and yet the resulting colloids are (iii) stable for months;^{13,18,20} (iv) to be easily implemented at laboratory scale and yet are scalable;^{18,19} (iv) to limit waste by limiting post-treatment of the materials obtained in non-viscous media (as opposed to alternative using polyols that require waste-generating washing steps typically in acids);²¹ (vi) to allow simple recycling of the solvent.¹⁹ These features overall lead to

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a better use of the precious metals leading for instance to more active (electro)catalysts.^{17–19,21,22}

Motivation

However, at the practical level, *e.g.* at large scale, high purity water might be too expensive to develop sustainable and truly green technologies. This consideration pushed us to explore alternatives to the state-of-the-art use of high purity water (mQ, Milli-Q® Millipore Water, 18.2 MΩ cm) for the synthesis of Au NPs. In most cases, syntheses performed in lower purity water do not lead to stable Au NPs colloids.^{10,13,16} Here, rather than completely ruling out the possibility to use low(er) purity water, we exploit the features of non-ideal case synthesis scenarios to achieve a fine size control over SF Au NPs obtained in alkaline ethanol–water mixtures at room temperature (RT) by tuning the amount of lower purity water. We also prefer the use of lower purity gold precursor and low purity stock solution of ethanol. It is also shown how the NPs obtained using relatively low grade chemicals are readily active catalysts for the reduction of 4-nitrophenol (4-NP) for water treatment²³ and to study and exploit various size-dependent effects at the nanoscale.

Experimental

A detailed account of the experimental methods, metrics and how the selected strategy complies with the principles of sustainable research is provided in ESI.†^{7,8,24,25}

General synthesis

An alkaline mixture of an alcohol and water leads to the formation of alkoxides that can play the role of reducing agents for the room temperature reduction of Au^{III} in HAuCl₄ to Au⁰ in NPs.^{18,26} Adding concentrated HAuCl₄ to an alkaline mixture of water and ethanol leads to the appearance of a grey color that then turns blue, deep purple, purple and finally red, see Fig. S1.† The red colour indicates the formation of spherical Au NPs *ca.* 10–20 nm in size. This synthesis has largely been documented elsewhere,^{13,18,27,28} and typical STEM and UV-vis data for the obtained materials using 0.5 mM HAuCl₄, 2 mM NaOH in 80 v% mQ water and 20 v% ethanol are reported in Fig. 1a and b (in red), respectively. The synthesis can easily be performed with relatively lower grade HAuCl₄, Fig. 1a, without significant benefits to use a higher grade precursor, see Fig. S2.† The synthesis is sensitive to the amount of base,^{18,29} but tuning the NaOH/Au molar ratio does not lead to a simple nor fine size control, as illustrated in Fig. S3.†

Size control

To assess the effect of the content of DI water, samples with 0.0 to 65.0 v% DI water were prepared (still with 20 v% ethanol and using otherwise mQ). Using higher amounts of DI water does not lead to any improvement to the synthesis but rather leads to unstable colloidal dispersions.¹³ The UV-vis spectra of the obtained colloidal Au NPs are reported in Fig. 1b. When

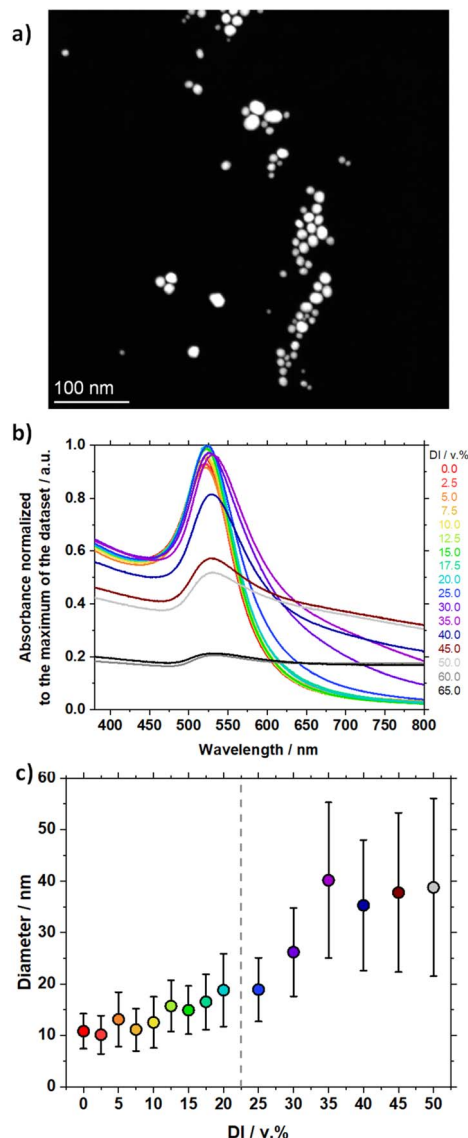


Fig. 1 (a) Illustrative STEM micrograph of Au NPs obtained 0.0 v% DI water. (b) UV-vis characterization of Au NPs colloidal dispersions obtained with different content of DI water, as indicated. (c) Diameter retrieved from STEM analysis as a function of the DI water content. The dotted vertical line marks the DI amounts after which the NPs tend to not be spherical anymore above *ca.* 22.5 v%. In all cases 0.5 mM HAuCl₄ and 2 mM NaOH were used for a total of 20 v% ethanol and 80 v% water (DI + mQ).

a controlled amount of DI water is added for the reactions, the UV-vis spectra of the Au NPs show distinctive features as a function of the DI water content, further detailed in Fig. S4.† At lower DI water amounts, a clear spr peak is observed around 520 nm and the absorption at high wavelengths is low. At higher DI water amounts the spectra show a spr at higher wavelengths and the absorption at high wavelengths is more pronounced.

The shift of the position of the surface plasmon resonance (λ_{spr}) towards larger wavelengths as the amount of DI water increases, illustrated in Fig. 1b and detailed in Fig. S4b,† indicates a size increase that is confirmed by STEM analysis and





The stability of the SF NPs is attributed to electrostatic stabilization. This argument is in line with zeta-potential measurements leading to values between -15 or -78 mV when the analysis is performed by inputting the properties of water or ethanol in the analysis software.¹⁸ These low values correlate well with the stability observed over time. A further argument for stabilization by electrostatic is that the cations used influence the stability in the decreasing order of stability $\text{Li}^+ > \text{Na}^+ > \text{K}^+$.¹⁸ The negative values from zeta-potential measurements could then suggest a role of the Cl^- anion in the stabilisation. We also observed that adding NaCl can lead to destabilization of the NPs although the NP remain stable for a relatively large range of NaCl concentrations.³⁰ Along those considerations, it cannot be excluded that pH is also likely to have an influence on the stability of the NPs, although an accurate measurement can be complex here, as detailed in ESI.† Preliminary results in this direction suggest that the pH drops upon adding HAuCl_4 from *ca.* 9–10 and stabilizes at a value typically around 4–5. This is in agreement with the expected equation of the reaction taking place, detailed elsewhere.¹⁸ However, using a pH probe often leads to destabilization of the colloids, which actually indirectly strongly suggests an electrostatic stabilization of the colloids. Finally, it cannot be excluded that oxidation products of ethanol such as acetaldehyde can also play a role in the stabilization, although surface species on the Au NPs remain challenges to probe and this is beyond the scope of this report.

The likely role of electrostatic stabilization explains why the size and stability of the NPs is sensitive to potential impurities¹⁰ and to the conductivity of the media used for synthesis which increases as the amount of DI water used increases, as detailed in ESI,† see for instance Fig. S14.†

Size effects

A first benefit of the size control achieved is to correlate various optical properties of the NPs to their size, illustrated in Fig. 2. As expected, lower λ_{spr} and lower A_{spr}/A_{450} values relate to smaller Au NP sizes.³⁴ However a closer look at the UV-vis spectra and A_{spr}/A_{450} values show that very low values, *e.g.* below 1.6, are not due to smaller size NPs but rather non-spherical NPs which is confirmed by STEM (samples with DI water amounts larger than 25 v%) as well as the relatively large corresponding λ_{spr} values. This explains why the A_{spr}/A_{450} value first increases as the amount of DI water increases (size effect), and then decreases as the amount of DI water keeps increasing (morphology effect) while the λ_{spr} values keep increasing, see Fig. S4 and S6.† In contrast, the relationship lower λ_{spr} values – smaller NP size is rather well maintained for all the samples in this study, see also Fig. S10.† Regarding other metrics, higher A_{380}/A_{800} and lower A_{650}/A_{spr} , also relate to smaller size and spherical Au NPs that leads to more stable colloids.

Catalysis

Au NPs obtained by the present RT SF strategy in alkaline water-ethanol mixtures are convenient and readily active catalysis demonstrated previously for electrocatalytic reactions, such as

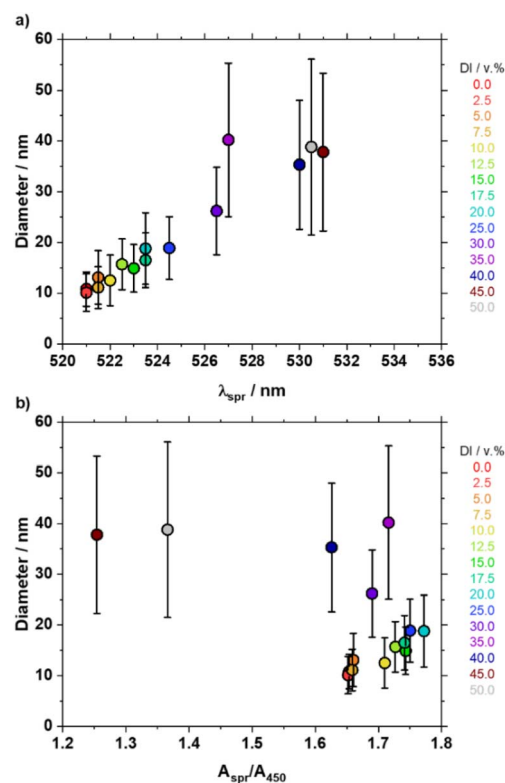
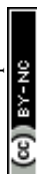


Fig. 2 Diameter as a function of (a) λ_{spr} and (b) A_{spr}/A_{450} for the Au NPs prepared using various amount of DI water, as indicated. In all cases 0.5 mM HAuCl_4 and 2 mM NaOH were used for a total of 20 v% ethanol and 80 v% water (DI + mQ).

the ethanol oxidation reaction (EOR), relevant for energy conversion in direct alcohol fuel cells.^{18,21,30} Here we explore the relevance of such NPs for water treatment. As an illustration and as a model system largely reported in the literature,^{23,35,36} the reduction of 4-NP in presence of NaBH_4 was also performed. The reaction can easily be monitored by following the decrease in the absorption at 400 nm in UV-vis spectra,^{37,38} as illustrated in Fig. S15a and detailed in Section S1.† The results are summarized in Table S5 in ESI† and details on the challenges to benchmark this reaction are provided elsewhere³⁸ and discussed in ESI, *e.g.* Fig. S15 and Section S11.† Presentation of the data including repeats and different normalization is proposed in Fig. S16–S18.†

The advantage of preparing size-controlled Au NPs is to perform studies of size-dependent effects that are usually pronounced at the nanoscale. The samples selected had a size of 10.8 ± 3.4 nm, 13.1 ± 5.3 nm, 12.5 ± 5.0 , 15.7 ± 5.0 , 18.8 ± 7.1 nm and 26.2 ± 8.6 nm and were obtained with 0.0 v%, 5.0 v%, 10.0 v%, 12.5 v%, 20.0 v% and 30.0 v% of DI water, respectively, as illustrated in Fig. 3 and see also S17.† As the NP size increases, the TOF for 4-NP reduction decreases, as expected from previous literature.³⁹ Similar results were obtained using NPs prepared using higher purity ethanol as stock solution of the alcohol, see Fig. S17.† Although the presence of alcohol in several v% was shown to slow down or even suppress the reduction of 4-NP,⁴⁰ it is here shown that traces of ethanol



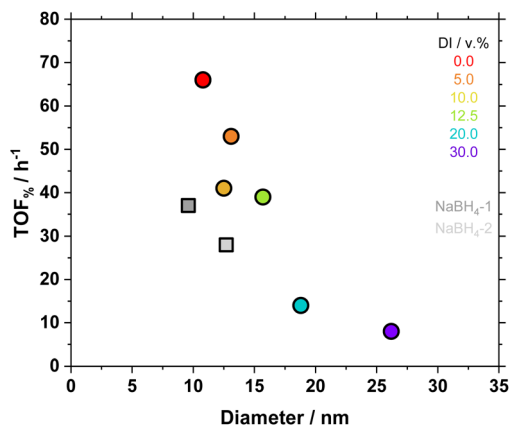


Fig. 3 TOF% as a function of the NP diameter for Au NPs prepared using different amounts of DI water or NaBH₄, as indicated.

from the synthesis of the Au NPs are not a challenge. A control experiment using directly HAuCl₄ – that can form NPs in presence of NaBH₄ – did not lead to a high TOF,⁴¹ see Fig. S16,[†] stressing the optimal strategy to use pre-formed NPs for the reaction. In previous reports, Au NPs prepared using only NaBH₄, water and a gold precursor were shown to be very active for the 4-NP reduction, in part due to the small size of the Au NPs obtained around 5 nm.³⁷ Au NPs were prepared by this method in the size range of 10 nm to allow a fair comparison. The Au NPs prepared using NaBH₄ showed lower TOF values than those estimated for the SF Au NPs obtained using ethanol–water mixtures with 0% DI water, or similar values to those obtained using up to 12.5 v% DI water despite the larger size of the latest. Overall, the results stress the promising catalytic activity of the here prepared SF Au NPs.

Conclusions

SF Au NPs are easily obtained at RT in alkaline water–ethanol mixtures. The synthesis is relatively green and (i) is performed with simple equipment, (ii) with low energy requirement (RT), (iii) requires only relatively benign chemicals, (iv) generates no or little waste during synthesis and/or for further use of the NPs given that low boiling point solvents are used.

It is shown that there is no need for high purity chemicals for a successful synthesis. Low(er) grade HAuCl₄, ethanol and water can be used to produce the Au NPs. The results stress the importance of controlling water purity for the RT SF Au NPs in alkaline water–ethanol mixtures. While it is typically considered as a disadvantage to use low(er) purity water, it is here used to develop an alternative strategy to those reported to date to tune the NP size and achieve a relatively fine size control. Controlling the DI water content in mQ water and 20 v% ethanol enables to achieve a size control in the range 10–30 nm. Increasing the DI water content leads to larger Au NPs.

The obtained Au NPs are readily relevant to study size effects in catalysis, for example for the 4-NP reduction. The smaller NPs lead to the more active catalysts for the 4-NP reduction. The NPs

obtained by the proposed method are more active than NPs obtained using for instance harmful chemicals such as NaBH₄.

The unique combination of a simple synthesis easily implementable by researchers without prior expertise in nanomaterial synthesis, that allows a simple yet fine control over Au NP size, and that leads to readily active NPs for catalysis, opens a range of opportunities. The presented synthesis leads to nanomaterials relevant for nanomaterial science,⁴² catalysis,⁴³ water/air treatment,⁴⁴ energy conversion,⁴⁵ addressing climate change,⁴⁶ sensing,⁴⁷ optics⁴⁸ and/or medicine,⁴⁹ and the concept is relevant for education.⁵⁰ It is expected that the simple and sustainable synthetic strategy reported will enable the holistic development of more sustainable nanotechnologies.

Data availability

The data supporting this article have been included as part of the ESI.[†]

Author contributions

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

Conflicts of interest

There are no conflicts to declare.

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