

PAPER



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Rapid, room-temperature, solvent-free mechanochemical oxidation of elemental gold into organosoluble gold salts†

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Gold is highly valued for a wide range of commercial and technological applications but is processed exclusively through highly aggressive and toxic solvents and/or reagents, ultimately yielding water-soluble salts that are difficult to separate from inorganic reaction byproducts. As a result, development of safer, cleaner processes that would enable gold processing in non-aqueous, organic solvent is an attractive technological goal. Here, we describe a methodology that simultaneously avoids aggressive reagents and enables gold extraction into a safe organic solvent. The methodology is based on solventless, mechanochemical oxidation of metallic gold with Oxone® in the presence of tetraalkylammonium halide salts, to directly, rapidly (within 30–60 minutes) and at room temperature convert gold metal into solid salts that are immediately soluble in pure organic solvents and aqueous alcoholic media. The organosoluble gold salts are easily separated from sulfate byproducts by direct extraction into the benign solvent ethyl acetate, which is also easily recycled for re-use, providing a strategy for gold activation and dissolution without any additional reagents for purification, such as cation exchange resins, salts, or chelating agents. Besides enabling direct extraction of gold into an organic solvent, the mechanochemically obtained organosoluble gold salts can also be readily used for further syntheses, as shown here by a two-step one-pot route to prepare air- and moisture-resistant Au(I) salts, and an improved synthesis of gold nanoparticles from bulk gold.

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Introduction

The development of efficient, safer and environmentally-friendly routes for the extraction and processing of rare elements is a major sustainability and technological challenge.^{1,2} Among rare metals, gold is notable for its commercial and technological applications, as well as fascinating chemical properties.^{3–9} The outstanding resistance to chemical attack means that gold processing and recycling rely on particularly aggressive and toxic techniques, requiring specialised

equipment, safety precautions, and waste management.^{10–12} As a result, gold mining and processing is a major cause of environmental damage,^{13–18} as methods for gold processing range from hot *aqua regia* (a 3 : 1 by volume mixture of concentrated hydrochloric or hydrobromic acid with nitric acid)¹⁹ and amalgamation with mercury at research and small manufacturing scales (*e.g.* artisanal and small-scale gold mining),^{20,21} to alkali metal fusions, alkaline cyanidation, and high-temperature chlorine gas oxidation at larger scales.^{22–24} All these methods eventually produce water-soluble gold species such as tetrachloroaurate(III) (AuCl₄[−]) salts that are further processed. Besides reagent toxicity, other hindrances in processing of such salts are the low volatility of water and the difficulty to separate gold salts from excess water-soluble reagents and reaction byproducts. As a result, there is much interest in new gold extraction strategies, including selective precipitation,^{25–27} chelating with macrocyclic hosts,^{28–30} or the use of 3D-printed scavenger filters.³¹ An important part of this effort is direct dissolution of gold into non-aqueous media,^{32–40} *e.g.* “organic *aqua regia*” (mixtures of thionyl chloride with pyridine or other organic bases),⁴¹ solutions of elementary halogens, nitrosonium salts, ionic liquids, or deep eutectic solvents.^{42–51}

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A methodology that simultaneously avoids aggressive reagents and enables gold extraction into a safe organic solvent has, however, remained out of reach.

We have previously shown that mechanochemistry, *i.e.* the use of mechanical agitation in the form of grinding or shearing, to conduct chemical reactions,^{52–61} offers a simple method to convert noble metals into water-soluble salts by using Oxone® (2 KHSO₅·KHSO₄·K₂SO₄) oxidant.⁶² While avoiding toxic reagents, this methodology, however, did not resolve the difficulty of separating the water-soluble noble metal salts and byproducts.

We now present a straightforward mechanochemical method that directly converts metallic gold into [AuX₄][−] derivatives that are soluble in organic solvents, permitting simple, one-step separation of gold salts from water-soluble oxidation by-products by extraction into a green solvent such as ethyl acetate (EtOAc) (Fig. 1a–c). The presented strategy rests on using tetraalkylammonium salts as halide sources, yielding organo-soluble salts that can immediately and in high yield (>90% in a single pass) be extracted into EtOAc. This permits the simple separation of the resulting gold salts from the sulphate-based oxidation by-products, without having to rely on any additional cation exchange or chelation strategies that would require additional solvents and/or reagents that would ultimately complicate handling of the wastewater stream or the purification of the gold salts. The ability to directly use tetraalkylammonium halides as reagents for gold activation is enabled by the mild nature of the mechanochemical process, compared to traditional gold activation strategies that are too harsh to permit the use of such organic reagents. The resulting

organoammonium tetrahaloaurate(III) salts are simply isolated by evaporation of the organic solvent, which is also readily recycled for reuse. The solid tetraalkylammonium haloaurates (III) can be directly redissolved in either pure organic media or aqueous ethanol (EtOH), making them suitable for diverse subsequent processing approaches, while remaining useful as precursors to more complex gold-based materials. The latter is evidenced through a one-pot mechanochemical process for the preparation of air- and moisture-resistant Au(I) derivatives, as well as a simplified route to gold nanoparticles (AuNPs).

Results and discussion

We first investigated the use of tetraethylammonium halides (TEAX, where X = Cl or Br) as halide sources: milling gold metal with 1.5 equivalents of Oxone® (*i.e.*, 3 equivalents of KHSO₅) and 4 equivalents of TEAX for 30 minutes yielded the corresponding [AuX₄][−] salts. The salts were then extracted by mixing with a 2 : 1 by volume mixture of EtOAc and water. The results were, however, poorly reproducible, most likely due to the highly hygroscopic nature of TEA⁺ salts (Table 1, entries 1–4) which led to water absorption and poor mixing, evident by aggregation of material on the milling media or vessel walls.

Increasing the milling time (Table 1, entries 6 and 7) or using freshly dried TEACl (Table 1, entries 8 and 9) enabled consistently high conversion. The resulting crude reaction mixtures were immediately analyzed by powder X-ray diffraction (PXRD), indicating the disappearance of Bragg reflections of gold, and the appearance of new reflections attributed to the desired tetraethylammonium haloaurate salts and potassium sulfate byproduct (Fig. 2a and also ESI Fig. S1, S2†). The conversion of gold into soluble salts was verified by reduction of the [AuX₄][−] species in aqueous methanol, followed by gravimetric analysis (Table S1, also ESI†).⁶⁴ Analysis of the crude mechanochemical reaction products by X-ray photoelectron

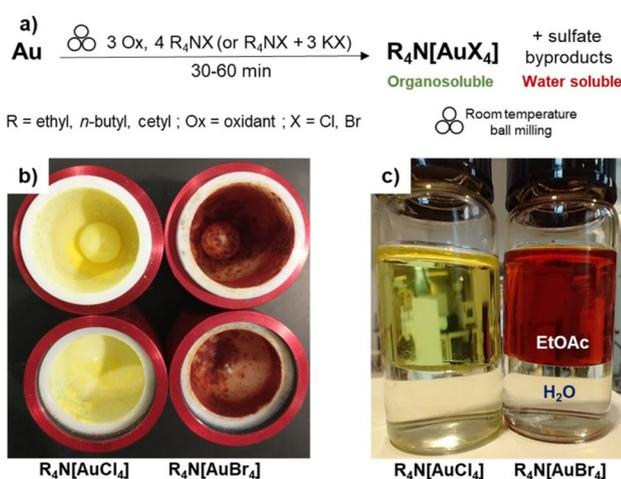


Fig. 1 (a) Schematic illustration of the herein presented mechanochemical strategy for the mechanochemical conversion of gold metal into organosoluble tetrahaloaurate(III) salts. Sulfate byproducts are products of Oxone reduction, such as K₂SO₄ and KHSO₄. Representative images of tetraalkylammonium tetrahaloaurate(III) salts obtained via the herein presented mechanochemical strategy: (b) raw products in zirconia milling jars and (c) after extraction into a mixture of EtOAc:water. Symbol for mechanochemical reactivity adapted from Rightmire and Hanusa.⁶³

Table 1 Results of exploring TEACl and Oxone® in the oxidation of metallic gold demonstrating the effects of using commercially received or dried tetraalkylammonium salts and of milling time^a

Entry	Milling time (min)	Conversion ^b (%)
1 ^c	30	51
2 ^c	30	75
3 ^c	30	60
4 ^c	30	89
5 ^c	30	42
6 ^c	60	93
7 ^c	60	90
8 ^d	30	94 ± 2
9 ^d	60	92 ± 4

^a Experiments conducted using 0.1 mmol Au metal, 4 equivalents of TEACl and 3 equivalents of the oxidant (see ESI†). ^b Conversion based on gravimetric determination of gold after extraction in EtOAc:water mixture (2 : 1 by volume). ^c TEACl used as received, each entry is an individual experiment. ^d TEACl recrystallised and dried prior to use, experiment conducted in triplicate, with the mean value shown.



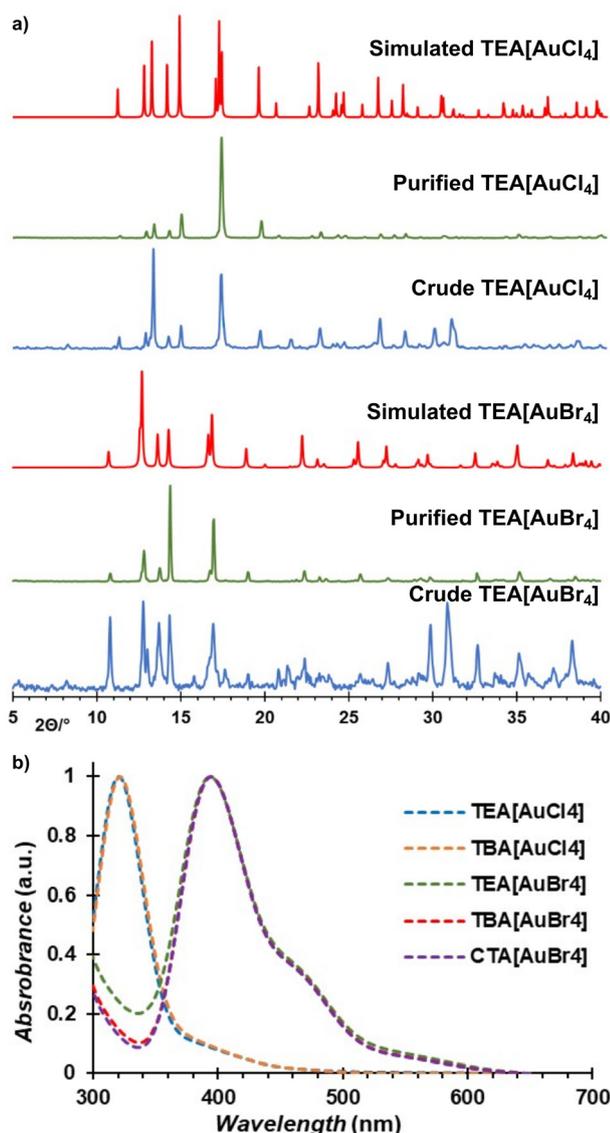


Fig. 2 (a) Comparison of PXRD patterns for TEA[AuCl₄] and TEA[AuBr₄]. The pronounced needle-like shape of crystals indicates that the relative intensities of X-ray reflections are affected by preferred orientation effects. (b) Normalised absorption spectra for the five tetraalkylammonium tetrahaloaurate salts in this study, recorded in EtOH.

spectroscopy (XPS) revealed the formation of Au(III) species, evident by 4f_{7/2} and 4f_{5/2} bands centered around 87 eV and 91 eV, respectively (Fig. S16 and S17[†]).⁶⁵ Au(I) species were also detected, as evident by 4f_{7/2} and 4f_{5/2} bands at 85 eV and 89 eV, respectively, explained by either degradation upon storage (*i.e.*, partial photoreduction of sample stored in a clear glass vial for several days) or upon exposure to the electron beam.

The pure oxidised gold compounds were readily isolated by biphasic extraction using a 1 : 2 by volume mixture of water and either EtOAc, chloroform, or dichloromethane, followed by separation and rotary evaporation of the organic phase, which allowed reuse of the organic solvent. This work-up was

optimised using EtOAc as a greener solvent choice (ESI, Table S2[†]), demonstrating a highly efficient (*ca.* 90–95%) transfer of gold into the organic layer in a single extraction step.⁶⁶ Overnight recrystallisation of the isolated solids from EtOAc produced diffraction-quality single crystals, and X-ray diffraction analysis confirmed the expected formula TEA[AuX₄].

The PXRD patterns of the crude and isolated materials were an excellent match with those calculated from single crystal data (Fig. 2a), with the disappearance of the characteristic Bragg reflections of the K₂SO₄ byproduct around 30° confirming successful purification by extraction (see ESI[†]).

The recrystallised tetraethylammonium tetrahaloaurates were also characterised by high-resolution mass spectrometry (HR-MS), nuclear magnetic resonance spectroscopy (NMR), Fourier-transform infrared attenuated total reflectance (FTIR-ATR), and ultraviolet-visible absorption spectroscopy (UV-Vis). Mass spectrometry confirmed the presence of Au(III) species, with [AuX₄][−] observed as the main ion in all cases (see ESI[†]). Analysis by FTIR-ATR and solution ¹H-NMR spectroscopy confirmed the persistence of the NEt₄⁺ cation in all cases (see ESI, Fig. S8, S9 and S14, S15[†]). Analysis by UV-Vis spectroscopy demonstrated the absence of product decomposition or formation of gold nanoparticles (AuNPs) during workup (Fig. 2b), with absorption maxima at 320 nm and 390 nm for the [AuCl₄][−] and [AuBr₄][−], respectively, which matches the expected literature values.⁶⁷ Next, we explored other tetraalkylammonium salt halide sources, such as tetrabutylammonium halides (TBAX, X = Cl, Br) that are commercially available and widely used as phase transfer agents.⁶⁸ No significant change in mechanochemical reactivity was observed compared to TEA analogues, though more consistent conversions of gold were obtained without pre-drying (89 ± 2% and 94 ± 4%, for TBACl and TBABr, respectively), in agreement with the less hygroscopic nature of TBA⁺ salts. Additionally, in exploring the mechanochemical reactivity with TBACl, the more hygroscopic of the two herein used TBA⁺ salts, it was observed that adding KCl as a secondary halide source further improved the mixing efficiency while still leading to the excellent conversion (89 ± 4%) of gold metal into TBA[AuCl₄] as the final product. Further optimisation of this procedure involving mixed halide sources revealed that using 1.1 equivalents of the tetraalkylammonium halide with three equivalents of KX (where X = Cl, Br) readily affords the desired product (ESI, Table S1[†]). Analysis by the aforementioned analytical methods confirmed the formation of the target salts TBA[AuCl₄] and TBA[AuBr₄] (Fig. 2b, also ESI[†]). X-ray diffraction-quality crystals were obtained for both compounds, revealing crystallographic parameters similar to those previously reported for TBA[AuCl₄].^{69,70} Notably, TBA[AuBr₄] (Fig. 3) is not isostructural to TBA[AuCl₄], and its structure was first investigated by Johnson and coworkers in 1981, but no atomic coordinates were available due to uncertainty in the space group and TBA⁺ disorder.⁷¹

With the TBA[AuCl₄] and TBA[AuBr₄] salts in hand, we further explored their mechanochemical reactivity. Previous reports indicated that such Au(III) salts could be selectively reduced to Au(I) analogues, allowing the preparation of



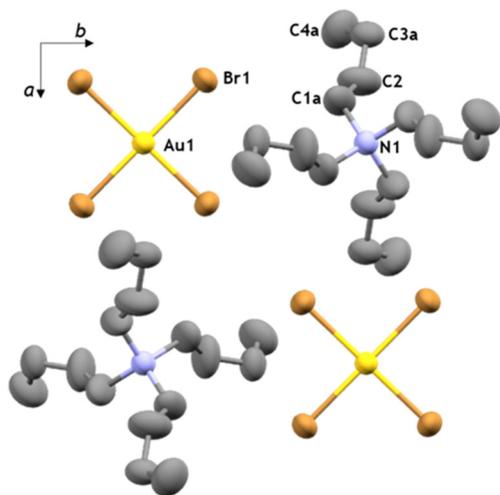


Fig. 3 Thermal ellipsoid representation of the contents of the crystallographic unit cell of TBA[AuBr₄], viewed down the crystallographic *c*-axis, with hydrogen atoms and the disorder affecting the *n*-butyl chains omitted for clarity.

air- and moisture-resistant Au(I) materials TBA[AuCl₂] and TBA[AuBr₂]. Specifically, Buckley *et al.* reported the reduction of TBA[AuCl₄] to TBA[AuCl₂] using sodium acetylacetonate (NaAcac) in a warm mixture of acetone and EtOH.⁶⁹ Inspired by this work, we investigated the mechanochemical reduction of freshly prepared TBA[AuX₄] salts by adding 1.1 equivalents of anhydrous NaAcac⁷² directly to the crude reaction mixture, followed by additional 30 minutes milling. The resulting two-step, one-pot mechanochemical procedure starting from metallic gold yielded pale yellow and orange-white solids for reactions containing TBACl and TBABr, respectively (Fig. 4a).

The PXRD patterns for the crude mechanochemical reaction mixtures (Fig. 4b and c) were a perfect match with those calculated for the TBA[AuCl₂] and TBA[AuBr₂] crystal structures.⁷³ Moreover, extraction of the crude reaction mixture with CDCl₃ confirmed the formation of the 3-halo-acetylacetonate byproduct by ¹H-NMR (Fig. 4a and ESI Fig. S13†). The TBA[AuX₂] salts were isolated by extraction of the reaction mixture with EtOH/acetone, followed by recrystallisation from EtOH, resulting in yield of 75 ± 4% and 80 ± 3% for TBA[AuCl₂] and TBA[AuBr₂], respectively.⁶⁹ Analysis of the crude milled reaction mixture by XPS also confirmed presence of Au⁺ in both cases (ESI, Fig. S21 and S22†).

Next, we targeted the mechanosynthesis of a gold(III) salt that is well known in AuNP synthesis, but is rarely isolated: cetyltrimethylammonium tetrabromoaurate.^{74,75} The required halide source, cetyltrimethylammonium bromide (CTABr) is a cationic surfactant frequently encountered in antiseptic formulations, and extensively used in the syntheses of Au nanomaterials.^{76–80} The CTA[AuX₄] salts have been previously noted as *in situ* formed precursors in AuNP synthesis upon combining an aqueous HAuCl₄ solution with a saturated solution of CTABr in toluene. Ball-milling of gold, Oxone and CTABr readily afforded the target salt CTA[AuBr₄] as a crystalline, bench-stable solid, with a conversion of 93 ± 2% after 30 minutes. High-quality single crystals of the salt were obtained by overnight recrystallisation from EtOAc and structural analysis revealed staggered chains of [AuBr₄][−] anions with short Br...Br contacts (3.4 Å) and layers of CTA⁺ with alternating hexadecyl chains (Fig. 5, also ESI†).

The direct mechanosynthesis of CTA[AuBr₄] enabled a simple two-step process to convert bulk metal into CTA-stabilised AuNPs using a protocol that, in contrast to the previously

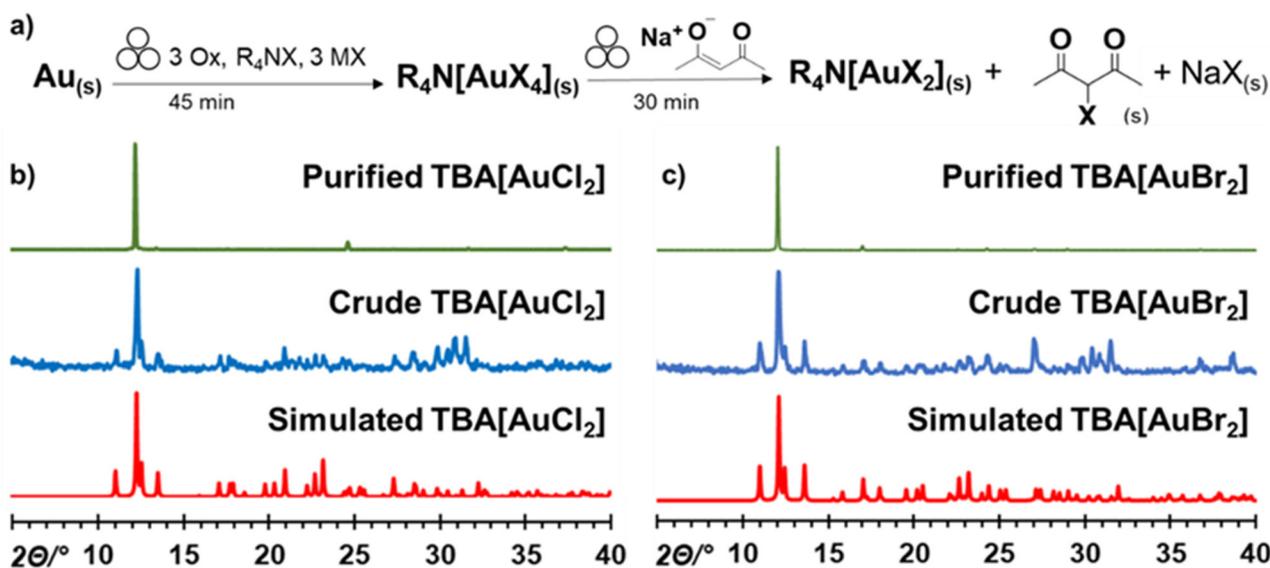


Fig. 4 (a) Reaction scheme for the one pot, two-step mechanochemical preparation of Au(I) salts from gold metal through a Au(III) salt reduced with sodium acetylacetonate. Comparison of PXRD patterns for TBA[AuX₂] after recrystallisation, the crude mechanochemical reaction mixture, and simulated for the corresponding crystal structures for: (b) X = Cl and (c) X = Br. The notably needle-like shape of crystals indicates that the relative intensities of X-ray reflections are affected by preferred orientation effects.



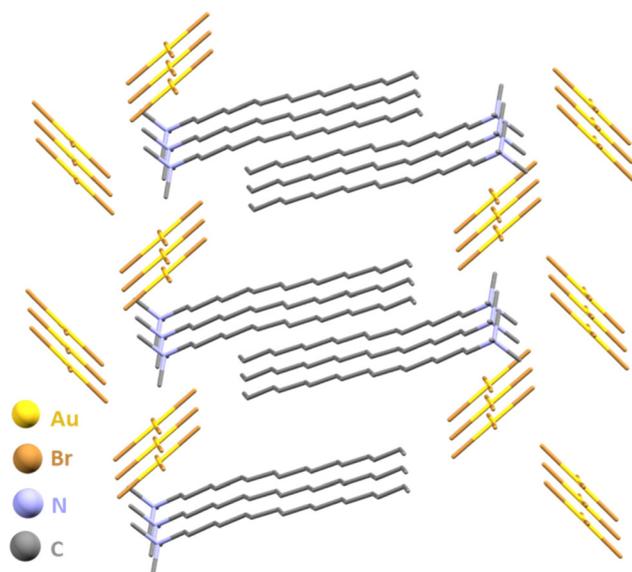


Fig. 5 Fragment of the crystal structure of CTA[AuBr₄], viewed along the crystallographic *a*-axis.

reported ones which assume complete phase transfer of reagents between water and toluene, enables the use of a precise amount of gold precursor.⁷⁵ Specifically, dropwise addition of aqueous NaBH₄ (10 mM) to a freshly prepared toluene solution of CTABr and mechanochemically prepared CTA[AuBr₄] (1.75 mM CTABr, 0.25 mM CTA[AuBr₄] in 10 mL) under vigorous stirring lead to an immediate color change from red/orange to a pale yellow, followed by a progressive change to ruby red/purple, the color remaining unchanged for hours if left unattended. Comparison of the absorption profile of the initial CTA[AuBr₄] solution in toluene and the final purple phase confirmed the formation of AuNPs characterised by the plasmonic band around 530 nm (Fig. 6). Dynamic light scattering (DLS) confirmed the formation of nanoparticles with an average diameter of 12 ± 2 nm (Fig. S28†).

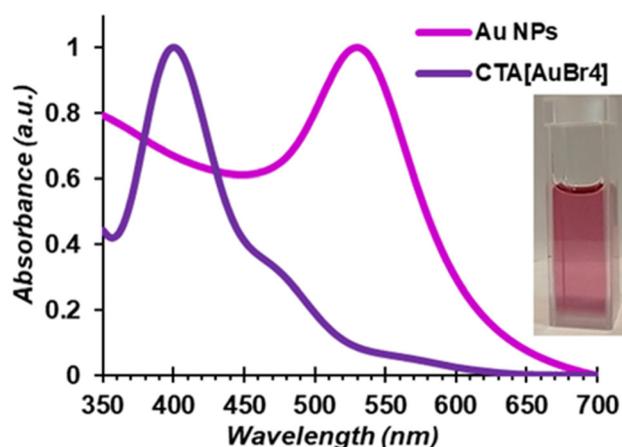


Fig. 6 Normalised absorption spectra of a CTA[AuBr₄] solution and of a solution of AuNPs obtained after addition of NaBH₄, recorded in toluene.

Conclusions

In summary, we reported a straightforward, rapid, and safe conversion of elemental gold into well-defined organosoluble Au(III) salts by using tetraalkylammonium halide salts as precursors. This enabled simple isolation of the organosoluble gold derivatives from water-soluble sulfate byproducts, without relying on additional reagents and strategies that might complicate processing or purification of the desired gold-based products and associated wastestreams. This strategy eliminates the risks associated with other ways of dissolving gold in organic media, such as handling pure halogens in organic solvents, while enabling reactions taking place at room temperature over a short period of time.³³ Control experiments (see ESI†) indicate that the mechanochemical halogenation of gold requires the use of ball milling, and proceeds hardly or not at all in aqueous suspension or by simple stirring. Further based on this straightforward methodology, we also introduce a promising two-step, one-pot mechanochemical methodology for the preparation of air- and moisture-stable Au(I) salts through the selective reduction of the freshly prepared Au(III) species using sodium acetylacetonate as a mild reducing agent. Finally, the use of CTABr as the bromide source in mechanochemical oxidation of gold enabled a simple, two-step procedure to transform bulk gold into AuNPs.

Overall, the work reported herein complements the widespread efforts dedicated to the synthesis and use of gold-based functional materials under mechanochemical conditions^{81–87} and opens the door for further development of safer and cleaner processes needed for the circular use of gold.^{88,89}

Author contributions

Jean-Louis Do: conceptualisation, investigation, visualisation, formal analysis, writing – original draft; Thomas Auvray: conceptualisation, investigation, visualisation, formal analysis, writing – original draft; Cameron B. Lennox: investigation, formal analysis, visualisation; Hatem M. Titi: investigation, formal analysis, visualisation; Louis A. Cuccia: resources, supervision; Tomislav Friščić: conceptualisation, writing – review & editing, resources, supervision. Jean-Louis Do and Thomas Auvray contributed equally.

Conflicts of interest

There are no conflicts to declare.

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