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

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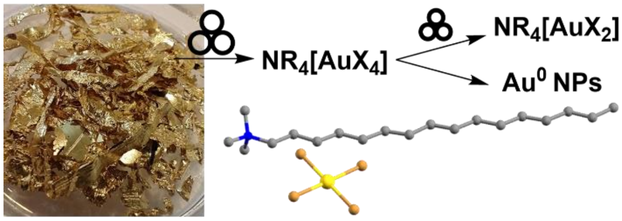

Abstract: Gold is highly valued for its wide-ranging commercial and technological use and is currently almost exclusively processed via aggressive reaction conditions that produce water-soluble salts. Oxidative mechanochemistry has previously been shown as a rapid, mild, and room-temperature alternative for chemically activating and transforming gold into water-soluble

species in the presence of potassium and ammonium halides. Demonstrated here is the extension of this strategy in the presence of tetraalkylammonium halides to directly and efficiently produce salts soluble in pure organic solvents and aqueous alcoholic media. This method affords gold salts that are rapidly and easily purified from byproducts using benign and easily recycled solvents and can be readily used for subsequent materials synthesis such as Au(I) salts and gold nanoparticles.

Introduction

Among the noble metals, gold is widely regarded for its commercial, industrial and academic uses.[1, 2] The high resistance of elemental gold to chemical attack requires it to be processed with especially harsh, aggressive, and toxic methods that require specialized equipment, safety precautions, and careful waste management.[3-5] These methods ranges from hot aqua regia (3:1 mixture of concentrated hydrochloric or hydrobromic acid and nitric acid) at academic and small industrial scales, or on larger industrial scales, to molten alkali metal fusions, alkaline cyanidation, and high temperature chlorination.[6-8] All these methods produce water-soluble Au(I) or Au(III) species that are readily transformed back to elemental gold *via* chemical or thermal reduction or electrolysis. The recovery of these soluble gold salts in a simple, rapid, and sustainable fashion for direct use is hindered by the low volatility of water, and the water-soluble nature of excess reagents and byproducts. There have been numerous recent attempts to address these problems, *e.g.*, by selective precipitation,[9, 10] chelation of aurate species using macrocyclic hosts,[11-13] 3D-printed scavenger filters,[14] direct one-pot conversion of elemental gold to organo-soluble complexes.[15-18]

We have previously shown that mechanochemistry, which encompasses the use of mechanical forces like grinding and shearing to initiate, sustain, and conduct chemical transformations,[19] is a simple, rapid, and environmentally-friendly method to convert noble metals such as Pd, Au, and Pt into water-soluble salts.[20] Specifically, ball milling of these raw precious metals, either alone or in a mixture, with mild oxidants such as potassium peroxymonosulfate ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, Oxone®), potassium persulfate ($K_2S_2O_8$), or calcium hypochlorite ($Ca(ClO)_2$) in the presence of simple halide salts results in tetrahaloaurate(III) $[AuX_4]^-$, tetrahalopalladate(II) $[PdX_4]^{2-}$ or hexahaloplatinate(IV) $[PtX_6]^{4-}$ derivatives (X = Cl, Br) with a preference for gold oxidization.[20]

Although this methodology permits rapid and simple synthesis of diverse coordination complexes, it remains limited by the need to isolate the desired water-soluble $[AuX_4]^-$ salts from sulfate byproducts by relying on repeated, consecutive, and slow crystallizations.

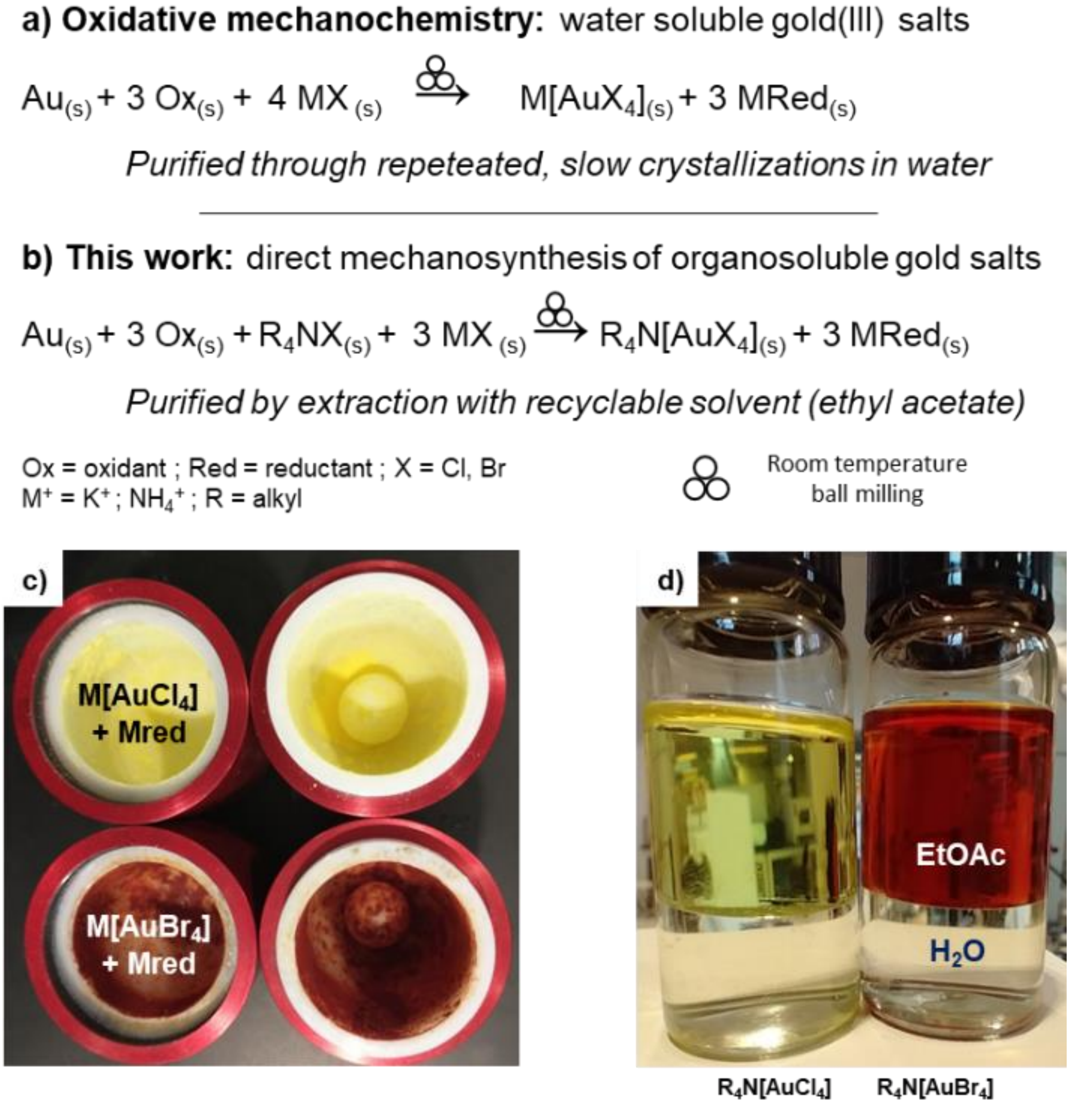

Figure 1. Previously (a) and herein (b) reported efforts in activation of metallic gold by oxidative mechanochemistry. c) Crude mechanochemical reactions in zirconia jars. d) Extraction of the mechanochemically prepared tetraalkylammonium tetrahaloaurate salts in ethyl acetate:water mixture.

Here, we demonstrate a mechanochemical method that directly converts metallic gold into simple $[AuX_4]^-$ derivatives that are soluble in organic solvents. The presented strategy rests on using tetraalkylammonium salts as halide source, yielding simple organo-soluble salts (Figure 1) that are readily extracted into organic solvents, permitting simple separation from solid sulfate byproducts. The resulting organoammonium tetrahaloaurate(III) salts are readily isolated by evaporation of organic solvents, that are also readily recycled for reuse. The ability to directly use tetraalkylammonium halides as reagents is enabled by the mild nature of the mechanochemical process, compared to traditional gold activation strategies that are sufficiently harsh to exclude the use of organic reagents. 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 the preparation of reasonably air- and moisture-stable Au(I) derivatives, as well as gold nanoparticles (AuNPs).

Results and discussion

We first investigated the use of tetraethylammonium halides (TEAX, where X = Cl or Br) as halide source: milling gold metal with 1.5 equivalents of Oxone$^{©}$ (i.e., 3 equivalents of $KHSO_5$) and 4 equivalents of TEAX for 30 minutes yielded the corresponding $[AuX_4]^-$ salts. The results were, however, poorly reproducible, most likely due to the highly hygroscopic nature of the TEA^+ salts (Table 1, entry 1-4) which led to water absorption and poor mixing evident by aggregation of the material on the milling media or vessel walls. Increasing the milling time (Table 1, entries 6-7) or using freshly dried TEACl (Table 1, entries 8-9) 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 elemental gold, and the appearance of new reflections attributed to potassium sulfate byproducts and the desired tetraethylammonium salts (Figures 2, S1, S2). The complete conversion of gold into soluble salts was verified by reduction of the $[AuX_4]^-$ species in aqueous methanol solution, followed by gravimetric analysis (Table 1, SI).[21]

Table 1. Results of exploring TEACl and Oxone® in the oxidation of metallic gold demonstrating the effects of using commercially received and dried tetraalkylammonium salts.[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 in triplicate, using 0.1 mmol Au metal, 4 equivalents of TEACl and 3 equivalents of the oxidant (see SI); [b] conversion based on gravimetric determination of gold; [c] TEACl used as received; [d] TEACl recrystallized and dried prior to use.

Analysis of the crude mechanochemical reaction products by X-ray photoelectron 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 (Figures S16-S17).[22] Au(I) species were also detected, which was evident by $4f_{7/2}$ and $4f_{5/2}$ bands at 85 eV and 89 eV, respectively, which was 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 oxidized gold compounds were isolated by biphasic extraction using a 1:2 by volume mixture of water and either chloroform ($CHCl_3$), dichloromethane (DCM), or ethyl acetate (EtOAc), followed by separation and rotary evaporation of the organic phase, which allowed reuse of the organic solvent. This work-up was optimized using EtOAc as a greener solvent choice (SI Table S2).[23] Overnight recrystallization of the isolated solids from EtOAc produced diffraction-quality single crystals, and X-ray diffraction analysis confirmed the expected formula $TEA[AuX_4]$. The two tetraethylammonium salts are isostructural, each crystallizing in the *P*2/*n* space group and presenting a linear arrangement of the $[AuX_4]^-$ anions along the *b* axis with short X···X interactions (3.380 Å and 3.416 Å for Cl and Br, respectively (Figures S23-S24).

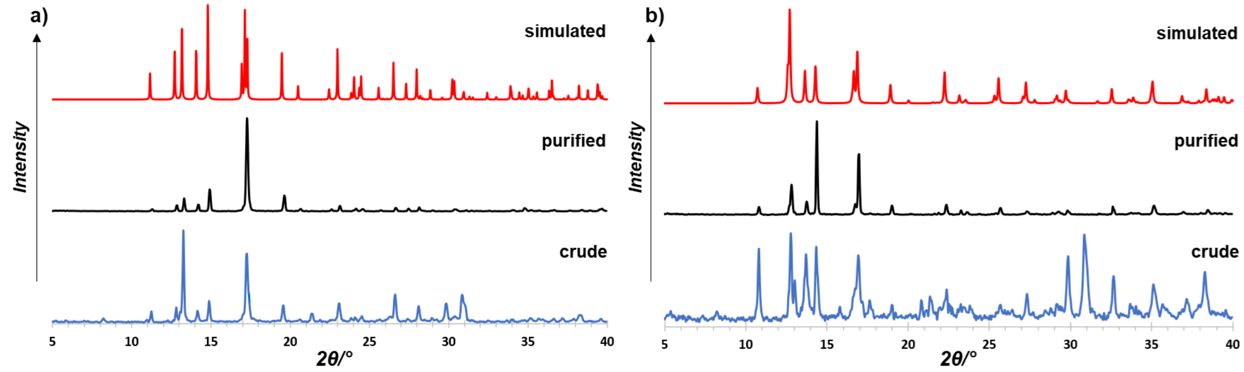

Figure 2. Powder X-ray diffraction patterns for: a) TEA$[AuCl_4]$ and b) TEA$[AuBr_4]$.

Comparison of the PXRD patterns of the crude and isolated materials with those calculated from single crystal data (Figure 2) showed an excellent match, high crystallinity, and confirmed the successful purification by extraction through disappearance of the characteristic K_2SO_4 Bragg reflections around 30°. The recrystallized tetraethylammonium tetrahaloaurates were also characterized 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 $[AuX_4]^-$ observed as the main ion in all cases (see SI). Analysis by FTIR-ATR and solution ^{1}H-NMR spectroscopy confirmed the persistence of the NEt_4^+ cation in all cases (Figures S8-S9, S14-S15). Analysis by UV-Vis spectroscopy demonstrated the absence of product decomposition or formation of AuNPs during workup (Figure 3) with absorption maxima at 320 and 390 for the $[AuCl_4]^-$ and $[AuBr_4]^-$, respectively, matching literature values.[24]

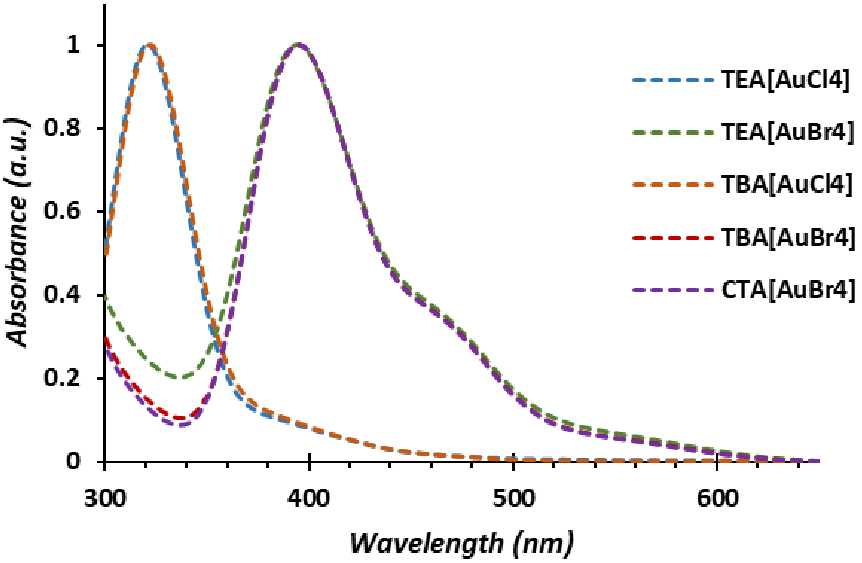

Figure 3. Normalized absorption spectra measured in EtOH for the five herein explored tetraalkylammonium tetrahaloaurate salts.

The low solubility of the tetraethylammonium salts in EtOAc led us to expand the study to other tetraalkylammonium salts, notably tetrabutylammonium halides (TBAX) which are widely commercially available and already commonly used as phase transfer agents.[25] No significant change in mechanochemical reactivity was observed compared to TEA analogues, though more consistent conversions were obtained, presumably due to improved mixing related to the less hygroscopic nature of TBAX 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 near quantitative conversion of gold metal into $TBA[AuCl_4]$ as the final product. Further optimization of this mixed halide source procedure revealed that using 1.1 equivalents of the tetraalkylammonium halide with 3 equivalents of KCl afforded the desired product.

Analysis by the aforementioned analytical methods confirmed the formation of the targeted salts TBA[AuCl$_4$] and TBA[AuBr$_4$] (Figure 3, also SI). Single crystals suitable for X-ray diffraction were isolated for both compounds, revealing similar crystallographic parameters to those previously reported for TBA[AuCl$_4$].[26, 27] Notably, TBA[AuBr$_4$] is not isostructural to TBA[AuCl$_4$]. The structure of TBA[AuBr$_4$] was first investigated by Johnson and coworkers in 1981, but no atomic coordinates could be provided due to to uncertainty in space group and severe disorder of TBA$^+$ cations.[28] Our data collection confirmed the proposed *P4/n* tetragonal space group with the gold and nitrogen atoms sitting on four-fold axis (Figure 4).

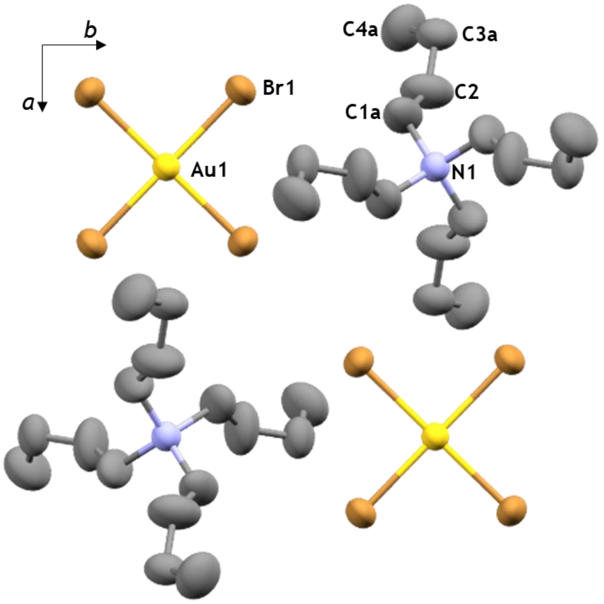

Figure 4. Thermal ellipsoid representation of the contents of the crystallographic unit cell of TBA[AuBr$_4$], viewed down the *c*-axis, with hydrogen atoms omitted for clarity, and only one of two disordered orientations shown for the *n*-butyl chains.

With the TBA[AuCl$_4$] and TBA[AuBr$_4$] salts in hands, it was possible to further explore their solid-state reactivity. Previous reports indicated that these Au(III) salts could be selectively reduced to their Au(I) analogues, allowing the preparation of TBA[AuCl$_2$] and TBA[AuBr$_2$] as air- and moisture-resistant Au(I) materials. Notably, Healy and coworkers reported the elegant reduction of TBA[$AuCl_4$] to TBA[$AuCl_2$] using sodium acetylacetonate (NaAcac) in a warm mixture of acetone and ethanol.[26] We thus investigated the mechanochemical reaction of freshly prepared TBA[AuX_4] salts by adding 1.1 equivalents of anhydrous NaAcac[29] to the crude reaction mixture, followed by additional 30 minutes milling. This simple two-step, one-pot procedure starting from metallic gold yielded pale yellow and orange-white solids for reactions containing TBACl and TBABr, respectively. The PXRD patterns of the crude mechanochemical reaction mixtures (Figure 5) were a perfect match with those calculated for the reported crystal structures of TBA[$AuCl_2$] and TBA[$AuBr_2$].[30] Moreover, extraction of the crude reaction mixture with $CDCl_3$ confirmed the formation by ^{1}H NMR of the 3-halo-acetylacetone byproduct (Figure S13). The TBA[AuX_2] salts were isolated by extraction of the reaction mixture with ethanol/acetone, followed by recrystallization in ethanol, as described in previous reports.[26] Analysis of the crude reaction mixture by XPS also confirmed appearance of Au^+ in both cases (Figures S21, S22).

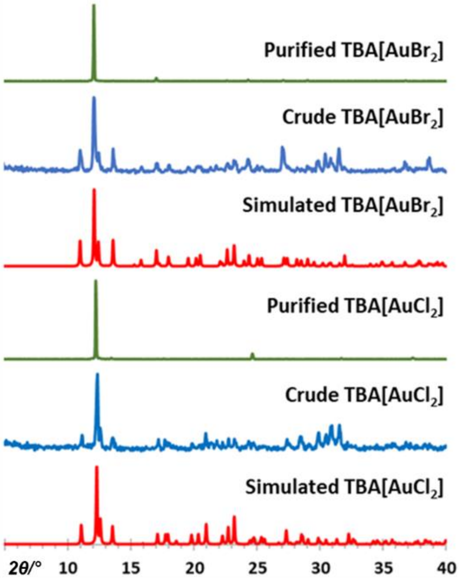

Figure 5. Powder X-ray diffraction patterns of the crude and purified (recrystallized) reaction mixture for TBA[AuX_2] (X = Cl, Br) and corresponding simulated patterns.

Next, we turned to a precursor salt that is highly popular but rarely isolated: cetyltrimethylammonium tetrabromoaurate. Indeed, cetyltrimethylammonium bromide (CTABr), a cationic surfactant frequently encountered in antiseptic formulations, is extensively used in nanoparticle (NP) synthesis. The CTA[AuX_4] salts have been previously noted as an *in situ* obtained precursor in AuNPs synthesis by combining an aqueous $HAuCl_4$ solution with a saturated solution of CTABr in toluene. Direct substitution of the more conventional TEA^+ and TBA^+ bromides with CTABr in the milling process readily afforded CTA[$AuBr_4$] as a crystalline, bench-stable solid. High-quality single crystals of this important precursor salts were obtained by overnight recrystallisation in EtOAc (Figure 6 and ESI) and structural analysis revealed staggered chains of $[AuBr_4]^-$ anions with short Br···Br contacts (3.4 Å) and layers of CTA^+ with alternating hexadecyl chains.

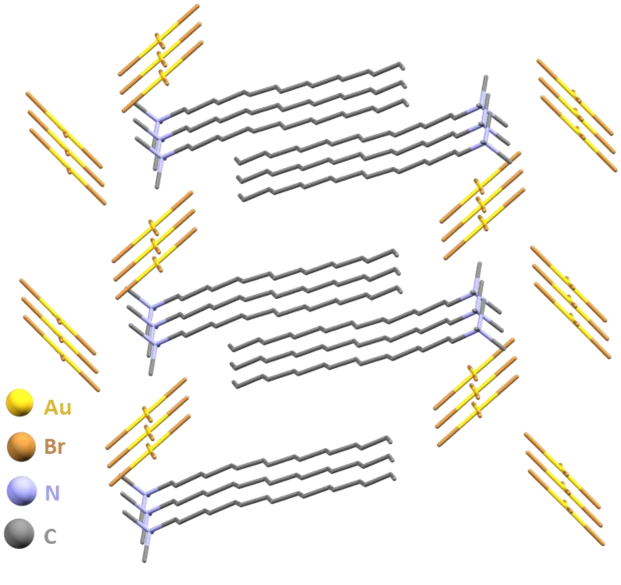

Figure 6. Stick representation of the crystal packing of ions in CTA[$AuBr_4$].

The CTA[$AuBr_4$] salt, directly synthesized from metallic gold, was readily applied for the synthesis of CTA-stabilized AuNPs in a protocol that, in contrast to the previously reported ones based on assuming complete phase transfer of reagents between water and toluene, enables the use of a precise amount of gold precursor.[31] Specifically, dropwise addition of aqueous $NaBH_4$ (10 mM) to a freshly prepared toluene solution of CTABr and CTA[$AuBr_4$] (1.75 mM CTABR, 0.25 mM CTA[$AuBr_4$] 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[$AuBr_4$] solution in toluene and the final purple phase, presented in Figure 7, confirmed the formation of spherical AuNPs characterised by the plasmonic band around 530 nm. Dynamic light scattering (DLS) confirmed the formation of nanoparticles with an average diameter of 12 ± 2 nm (Figure S28).

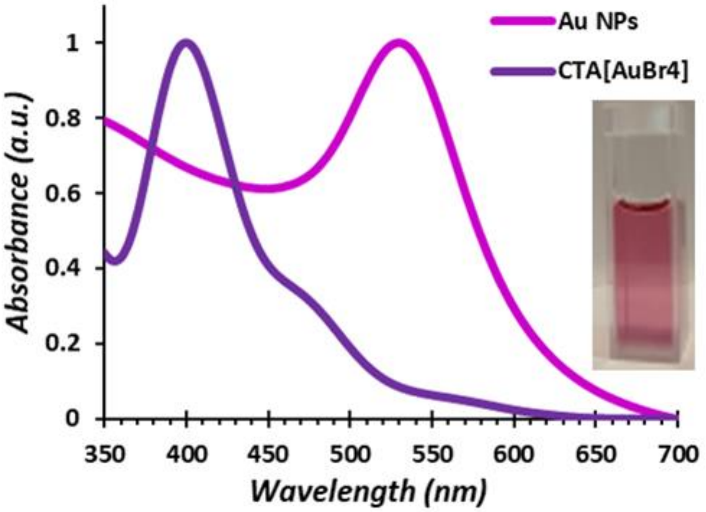

Figure 7. Normalized absorption spectra in toluene of a CTA[$AuBr_4$] solution and of the Au NPs suspension obtained after addition of $NaBH_4$.

Conclusions

In summary, we have improved our previous use of mechanochemistry for the simple, rapid, and safe conversion of elemental gold into well-defined Au(III) salts by targeting tetraalkylammonium salts as precursors, enabling simple isolation of the gold derivatives from water-soluble byproducts. This strategy eliminates the risks associated with handling pure halogens in organic solvents and delivers enhanced synthetic conditions with the reaction taking place at room temperature over a short period of time.[18] Additionally, we 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. The work reported herein complements the widespread efforts of others dedicated to the synthesis and utilization of gold-based functional materials under mechanochemical conditions[32-38] and opens the door for further developments towards a circular use of gold thanks in-part to improved mechanochemical recovery methods.[39, 40]

Supporting Information.

Material and methods, experimental conditions, ^1H NMR spectra, ESI HR-MS data, FT-IR spectra, detailed X-ray diffraction analysis, Powder X-ray diffraction analysis and XPS data.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally to this work.

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