Nano Futures

LETTER • **OPEN ACCESS**

Alkynide-stabilised gold nanoparticles: a synthetic investigation

To cite this article: Paige K Summers and Andrew M McDonagh 2025 *Nano Futures* **9** 021001

IOP Publishing *Nano Futures* **9** (2025) 021001 https://doi.org/10.1088/2399-1984/addb18

NANO
FUTURES

OPEN ACCESS

RECEIVED
13 May 2025

ACCEPTED FOR PUBLICATION
20 May 2025

PUBLISHED
2 June 2025

LETTER

Alkynide-stabilised gold nanoparticles: a synthetic investigation

Paige K Summers and Andrew M McDonagh[*]

School of Mathematical and Physical Sciences, University of Technology Sydney, Broadway, Ultimo, NSW 2007, Australia
[*] Author to whom any correspondence should be addressed.

E-mail: Andrew.McDonagh@uts.edu.au

Keywords: gold nanoparticles, synthesis, alkyne, alkynide

Supplementary material for this article is available online

Abstract

Alkyne compounds have emerged as promising stabilising ligands for gold nanoparticles, with potential applications in sensing, catalysis and biological imaging. Several examples of alkynide-stabilised gold nanoparticles have been reported although most use a mixed-ligand system that requires additional stabilising agents. Thus, a facile and size controllable synthesis of gold nanoparticles stabilised exclusively with alkyne compounds is highly desirable. Here we report dec-1-ynide@AuNPs that were synthesised by reduction of a Au(I) dec-1-ynide complex to give nanoparticles with diameter of ∼3.4 nm and are stable in air for up to 2 months. ^{1}H NMR spectra indicate that the particles have a shell that contains gold(I) species surrounding a core of gold(0) atoms. The synthetic technique was modified to increase the size of the AuNPs but the larger AuNPs were stabilised predominantly by tetraoctylammonium bromide (TOAB). Methods that utilised reduction of Au(III) chloride with the phase transfer agent TOAB resulted in bidisperse AuNPs with diameters of ∼9 nm and ∼3 nm. Variation of the synthesis conditions did not have a significant effect on the particle sizes and residual TOAB was required to maintain particle stability.

1. Introduction

Gold nanoparticles (AuNPs) are typically stabilised by ligands where molecular composition and conformation play a critical role in electronic and optical characteristics, stability and reactivity [1–3]. Ligands that have been traditionally used to stabilise AuNPs include citrate [4, 5], thiol [6], phosphine [7], and amine ligands [1, 8], polymers [9], with compounds such as thioureas [10, 11], N-heterocyclic carbenes [12–14], and of particular relevance to the current work, alkynes, being more recently investigated [15–17].

Alkynes have emerged as an important class of ligands to stabilise AuNPs [15, 16] as well as gold nanoclusters (AuNCs)[18–21] (we use the terminology [22] that nanoclusters have diameters ⩽2 nm). Alkyne ligands provide additional opportunities to tune the optical [23, 24] and catalytic properties [15, 25] of AuNPs and afford a strong Au-ligand bond [26, 27].

Alkyne compounds are useful to covalently bond biological molecules gold surfaces to avoid interference from biological thiols [28] and impart high electrochemical transmittance to improve signal transmission during sensing processes [29–31]. AuNPs functionalised with alkynes are sensitive detectors of hydrogen peroxide and streptavidin proteins, showing long term stability and resistance to decomposition under harsh conditions [16]. They exhibit stability in high salt conditions, a range of pH values, allowing reliable detection in biological applications [32]. They have also demonstrated some excellent catalytic properties [15, 33].

Alkyne-stabilised AuNPs can be synthesised by a variety of methods. Ligand exchange reactions have been used where the particle core is formed using another stabilising group and then exchanged for the alkyne ligand. For example, polyvinylpyrrolidone (PVP) stabilised AuNCs can undergo ligand exchange to give phenylacetylene, 1-octyne, or 9-ethynyl-phenanthrene stabilised particles [19, 20]. Interestingly, PVP@AuNPs with diameters >4 nm were reported to be unable to be synthesised due to a proposed size-specific reactivity. Recently, acetylide stabilised AuNPs with diameters greater than 4 nm were synthesised in the presence of PVP [15], although in this case the PVP stabiliser was not entirely displaced by the incoming alkyne ligands. Citrate-stabilised AuNPs have been shown to undergo ligand exchange with alkyne ligands to produce phenylacetylene-polyethylene glycol (PEG) stabilised NPs [33] or alkynylated biotin stabilised particles [16]. Thiolate-stabilised AuNPs can exchange thiol ligands for alkyne ligands under certain conditions [16]. Using alkynide anions (either lithium- or gold(I)-phenylacetylide) resulted in either partial and full ligand exchange on small (Au_{25}) NCs [34].

Direct synthesis methods have also been explored. A one-pot method involving synchronous nucleation and passivation added all reagents (metal salt, ligand, and reductant) simultaneously albeit with less kinetic and yield control [35, 36]. The popular Brust–Schiffrin method [37] (used to prepare thiol-stabilised AuNPs) has been modified to use 1-dodecyne as a stabiliser and yielded particles with diameters of 4.5 and 2.6 nm [17].

Direct reduction of Au(I)-alkynide complexes has been used to synthesise alkyne-protected AuNCs with well-defined sizes and structures [18, 21, 36, 38–41] albeit with low yields although a recent synchronous nucleation and passivation strategy has been applied to give AuNCs in up to 70% yield [42].

As part of our investigations into the sintering behaviour of AuNPs [43–49] that include alkynide -stabilised AuNPs (to probe the effect of the strong Au–C bond), we required syntheses that produce alkynide-stabilised AuNPs in reasonable yield and quantities, with well-defined ligand environments. We found that several existing synthetic methods were not suitable for this task, or that they resulted in AuNPs that retained additional stabilising agents. With only a few reported methods for the synthesis of alkynide-stabilised AuNPs, a facile synthesis that produces AuNPs stabilised only with alkyne ligands and with a reasonably narrow size distribution was critical to ensure reproducible behaviour. Such a method would also be valuable in applications such as sensors and catalysis (although not the focus of the current work) where activity can be dependent on NP sizes and distributions [50–53].

Here we report our investigations into the synthesis of alkyne-stabilised AuNPs using methods based on the Brust–Schiffrin synthesis as well as via an Au(I)-alkynide precursor. We show that syntheses that use Brust–Schiffrin conditions adapted for alkynes do not yield AuNPs stabilised solely with alkyne ligands. However, when Au(I)dec-1-ynide was used as a precursor, we obtained AuNPs with diameters 2–4 nm that are stabilised with only alkyne ligands.

2. Results and discussion

A synthesis AuNPS was conducted using a tetraoctylammonium bromide (TOAB)-assisted phase transfer reduction method (Method A) and 1-decyne. This general method is commonly used to prepare thiol-stabilised AuNPs (the Brust–Schiffrin method) [37]. As we show below, this method requires that the phase transfer agent (in this case TOAB) not be removed for the particles to remain stable when alkyne was used as a stabilising ligand.

AuNPs were synthesised by first transferring $AuCl_4^-$ into toluene from water using TOAB as phase-transfer agent. 1-Decyne was added and the Au(III) was reduced using $NaBH_4$ to give a deep red dispersion of AuNPs. The resultant AuNPs were characterised by ultraviolet-visible (UV–vis) absorption spectroscopy, transmission electron microscopy (TEM) and proton nuclear magnetic spectroscopy (^{1}H NMR).

The UV–vis spectrum (see figure 1(a)) contains a plasmon resonance band with a peak at 525 nm, consistent with previous reports [17]. TEM (figure 2(a)) showed nanoparticles with size ranges of 9.4 ($\pm$3) nm and 4.0 ($\pm$1) nm (figure S1(a)). These were stable as powders for up to two months. After two months, when the powders were dispersed in chloroform, a deep blue colour was observed, indicating the formation of large and irreversible aggregates that precipitated within 12 h.

The ^{1}H NMR spectrum of the AuNPs prepared by Method A (figure S2) contains signals arising from TOAB (assigned by comparison with the spectrum of pure TOAB, figure S2). Signals associated with the alkyne ligand are not apparent. ^{1}H NMR spectra also revealed that after multiple (up to 16) washes with acetonitrile, as well as mechanical agitation, residual TOAB could not be removed. Interestingly, previous research that used ligand exchange methods (PVP or PEG exchanged for acetylide ligands) to form acetylide-protected AuNPs with diameters >4 nm reported residual PVP or PEG in the resultant nanoparticles [15, 33]. However, smaller nanoparticles (diameter <2 nm) have been stabilised solely by acetylide ligands via a ligand exchange with PVP [19]. We therefore investigated modifications to Method A in an effort to synthesise smaller AuNPs (i.e. diameters <4 nm). Several variations to reaction conditions of the Brust–Schiffrin method have been shown to yield thiolate-stabilised AuNPs with diameters as small as $\sim$1.5 nm [54, 55]. We applied these variations to the synthesis of alkyne-stabilised AuNPs such that the 1-decyne:$HAuCl_4$ mole ratio was increased from 1:1 to 64:1, the reaction temperature reduced to ~-10 °C, and the time period for $NaBH_4$ addition was decreased from 30 s to $\sim$1 s (Method B).

The UV–vis spectrum (figure 1(b)) of AuNPs obtained using Method B contains a plasmon resonance band with a maximum at 517 nm, suggesting only a small reduction in particle size (compared to 525 nm for Method A) [1]. TEM images (figure 2(b)) showed that the size of the gold core for Method B have two

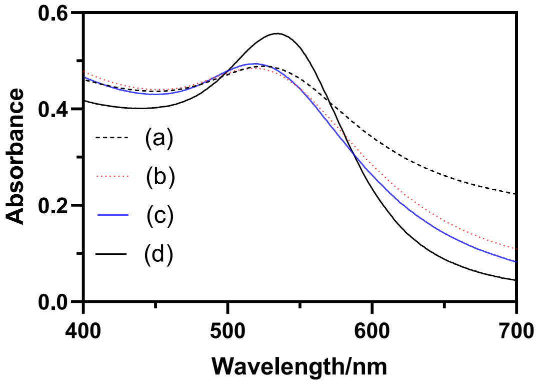

Figure 1. UV–visible spectra of: (a) AuNPs synthesised using Method A, (b) AuNPs synthesised using Method B, (c) AuNPs synthesised using Method C (washed with water only), (d) AuNPs synthesised using Method E.

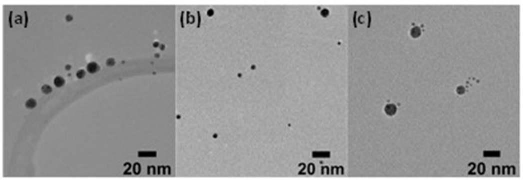

Figure 2. TEM of (a) Dec-1-ynide/TOAB-stabilised AuNPs (Method A); (b) Dec-1-ynide/TOAB-stabilised AuNPs (Method B); (c) TOAB-stabilised AuNPs (Method C).

distinct sizes of 9.1 (±0.5) nm and 3.5 (±0.7) nm (figure S1(b)), which are also similar to those prepared using Method A. Likewise, the ^{1}H NMR spectrum of AuNPs synthesised using Method B was similar to that of particles prepared by Method A. Thus, the modifications to the synthetic method did not yield smaller nor TOAB-free AuNPs.

To explore whether the addition of alkyne was at all necessary in these methods, AuNPs were synthesised using a similar procedure except the addition of 1-decyne was omitted (Method C) [56]. This reaction yielded similar deep red dispersions of AuNPs but were significantly less stable than the alkyne-containing dispersions. The as-synthesised dispersions precipitated within 24 h, indicating aggregation. Washing the particles resulted in rapid aggregation and solvent removal gave a solid material that could not be re-dispersed. The UV–vis spectrum (figure 1(c)) of the as-synthesised TOAB@AuNPs, contains a plasmon resonance band at 519 nm and TEM images (figure 2(c)) show two distinct size ranges of 10.8 (±2) nm and 3.1 (±0.6) nm (figure S1(c)), similar to the AuNPs synthesised by Methods A and B. The ^{1}H NMR spectrum of the TOAB@AuNPs (figure S2) was also similar to those of particles prepared by Methods A and B. Thus, we conclude that stable AuNPs synthesised by this modified Brust–Schiffrin method must contain both alkyne and TOAB stabilising ligands and that particles with $d < 5$ nm are not readily accessible by this route.

$$\mathrm{HAu(III)\,Cl_4 + 3HSR \rightarrow (Au(I)SR)_n + RS\text{ - }SR + 4HCl} \tag{1}$$

$$\mathrm{(Au\,(I)\,SR)_n \xrightarrow{NaBH_4} RS@Au\,(0)\,NPs} \tag{2}$$

$$\mathrm{HAu^{III}Cl_4 + HC \xrightarrow{NaBH_4} RC \equiv C@Au^0NPs.} \tag{3}$$

In our quest for alkyne-stabilised AuNPs with diameters <4 nm, we reasoned that one factor that influenced the larger particles that result from Methods A-C (compared to thiolate-stabilised analogues) involves the pathway of reactions that lead from Au(III) to Au(0) [57]. When $HAuCl_4$ is reacted with thiol, there is an immediate reduction of Au(III) to Au(I) and an associated oxidation of the thiol, equation (1). Upon introduction of $NaBH_4$, there is then rapid reduction of Au(I) to Au(0) to form NPs, equation (2). In contrast, addition of $HAuCl_4$ to a terminal acetylene does not facilate reduction of the Au(III) to Au(I). Thus, when $NaBH_4$ is added to the $HAuCl_4$ and alkyne mixture, a three-electron process must occur to give Au(0) NPs, equation (3), as well as breaking the quite stable (relative to the thiol H–S bond) H–C alkyne bond [58]. To mimic the reduction process utilised in thiol-stabilised AuNPs, a Au(I)-alkynide complex was synthesised

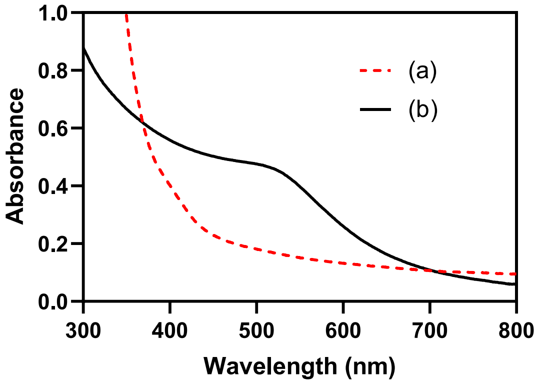

Figure 3. UV–visible spectrum of (a) gold(I)dec-1-ynide; (b) dec-1-ynide@AuNPs (Method D).

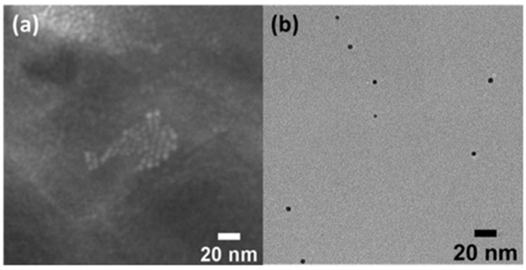

Figure 4. (a) SEM and (b) TEM images of dec-1-ynide@AuNPs via Method D.

and subsequently reduced to form AuNPs. This strategy has been utilised in synthesis of alkynide-protected NCs stabilised using a range of alkynes [21, 39].

In this work, dec-1-ynide-stabilised AuNPs were synthesised using the gold(I)dec-1-ynide complex. The gold(I)-complex was dissolved in toluene together with the phase-transfer agent, TOAB. Aqueous $NaBH_4$ was added and the organic phase became brown in colour, indicating the formation of AuNPs (Method D). The resultant AuNPs were cleaned by precipitation with methanol and washed twice with addition acetonitrile. The washed nanoparticles could be re-suspended in chloroform or toluene without aggregation, unlike those prepared by Methods A–C. The NPs were stable for up to two months as powders.

The UV–vis spectrum (figure 3(b)) contains an absorbance shoulder at ~520 nm and is similar to the spectrum of octyn-1-ide stabilised AuNPs with diameters of ~3.2 nm (prepared via ligand exchange with PVP) [19]. The surface plasmon band indicates that the diameters of the AuNPs are smaller than those synthesised by Methods A–C. The spectrum of the dec-1-ynide@AuNPs is markedly different to that of the gold(I)dec-1-yne complex (figure 3(a)).

Scanning electron microscopy (SEM) (figure 4(a)) of AuNPs synthesised using Method D revealed average diameters of ~4 nm. TEM images (figure 4(b)) indicate a size range of 3.4 (±0.4) nm (figure S1(d)).

^{1}H NMR spectra, (figure 5(b)), contain no signals from residual TOAB nor from 1-decyne. Interestingly, the ^{1}H NMR spectrum of dec-1-ynide@AuNPs is very similar to that of the gold(I)dec-1-ynide complex. In both spectra, figure 5(a) and (b), a triplet at 2.62 ppm is assigned to the protons at the C3 positions (the position adjacent to the C≡C), a quintet at 1.62 ppm is assigned to the protons at C4, and a multiplet at 1.42 ppm is assigned to the C5 protons.

Peak broadening of signals assigned to protons close to the gold surface has been reported for thiol-stabilised AuNCs [55, 59, 60]. Previous work investigating phenylacetylide-stabilised AuNCs, formed from a gold(I)phenylacetylide compound, proposed (based on x-ray photoelectron spectroscopy data) a Au(0) core surrounded by Au(I) species but no NMR data were reported [21]. ^{1}H NMR spectra of AuNPs stabilised with N-heterocyclic carbenes showed remarkable similarly to that of the precursor Au(I) carbene complex, suggesting also a Au(0) core with a Au(I) shell [61]. In contrast, 4-pentyl phenylacetylene-protected gold clusters of ~1.5 nm prepared via ligand exchange with PVP-stabilised AuNCs show peak broadening on the phenyl and methylene peaks [20]. We therefore propose that the dec-1-ynide@AuNPs synthesised in the current work are of similar composition. That is, they contain a

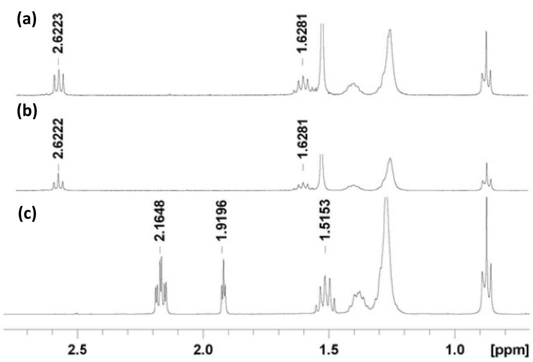

Figure 5. ^{1}H NMR spectra of (a) gold(I)dec-1-ynide; (b) dec-1-ynide@AuNPS (Method D); (c) 1-decyne.

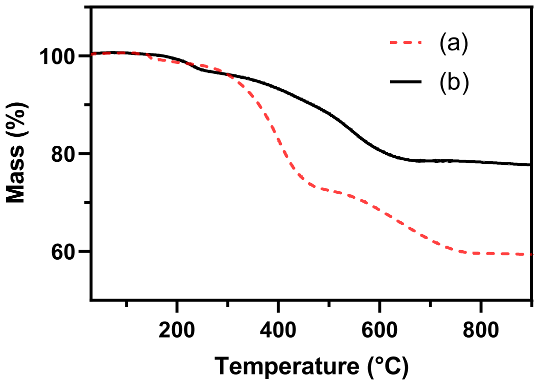

Figure 6. TGA for (a) gold(I)dec-1-ynide; (b) dec-1-ynide@AuNPs (Method D).

significant amount of Au(I) species at the particle surface. Future studies using x-ray photoelectron spectroscopy may shed further light on the nature of the particle surface composition.

Thermogravimetric analysis (TGA) data for gold(I)dec-1-ynide and dec-1-ynide@AuNPs are shown in figure 6. A mass loss of 42% was observed for gold(I)dec-1-ynide upon heating to 1100 °C. This agrees with the calculated value of 41%. For the dec-1-ynide@AuNPs, a mass loss of a 22% was measured. For particles with radii of 1.7 nm (and thus a mass of gold of 3.98×10^{-19} g) this implies 1.12×10^{-19} g of ligand per NP, or 491 ligands per nanoparticle. Thus, the surface coverage of ligands on the NPs is calculated to be 13.5 ligands/nm^2. This number is similar that of AuNPs stabilised by NHCs with a reported Au(I) shell over an a Au(0) core [62], with a surface density of 13.1 ligands nm^{-2}.

The dec-1-ynide@AuNPs showed ligand loss over two distinct steps commencing at ~190 °C and ~247 °C. A similar pattern was reported for AuNCs stabilised with phenylacetylene-stabilised AuNCs [21] as well as N-heterocyclic carbene-stabilised AuNPs [61].

Having developed a synthesis of decyn-1-ide@AuNPs with diameters of <4 nm, a synthesis of dec-1-ynide@AuNPs with diameters >4 nm was explored. A modified version of Method D was performed to increase the AuNP diameters. The amount of reducing agent was halved compared that of Method D, the time for addition of the reducing agent was increased to 60 s, and the temperature was maintained at 23 °C. The ^{1}H NMR spectrum of the AuNPs prepared by Method E (figure S2) contains signals similar to the spectra of AuNPs prepared using Methods A-C. This method (Method E) resulted in a deep purple-red solution, with UV–vis spectrum containing a plasmon resonance band with a maximum at 535 nm (figure 1). These data indicate that, unlike Method A, Method D can be modified to influence the size of the prepared nanoparticles.

3. Conclusion

Several pathways into alkynide-stabilised AuNPs have been explored. Stable dec-1-ynide@AuNPs have been synthesised by reduction of a Au(I)dec-1-ynide complex to give NPs with diameter of ~3.4 nm (Method D). ^{1}H NMR spectra suggest that the particles have a shell that contains gold(I) species. This new synthetic method provides an accessible route into AuNPs that are stabilised with only alkyne ligands with a well-defined size range. This method could be investigated in future work to explore the range of compatible alkyne compounds. This synthetic technique was modified to change the size of the AuNPs (Method E), but the larger AuNPs were found to be stabilised predominantly by TOAB.

Methods that utilised reduction of Au(III) chloride with the phase transfer agent TOAB (Methods A–C) resulted in bidisperse AuNPs with diameters of ∼9 nm and ∼3 nm. This aspect should be considered by researchers working with such AuNPs as the role of the surfactant may not have been apparent in previous work. Variation of the synthesis conditions did not have a significant effect on the particle sizes. All of the AuNPs prepared by Methods A–C had similar organic profiles with TOAB required to maintain particle stability. AuNPs prepared using only TOAB as stabiliser (Method C) yielded NPs with lower stability than those that also utilised 1-decyne (Methods A-B).

4. Experimental

4.1. Materials and methods

1-Decyne, TOAB, sodium borohydride, triethylamine, dimethylsulfide, methanol, acetonitrile, deuterated chloroform ($CDCl_3$) were purchased from Sigma-Aldrich and used as received. Toluene and diethyl ether (ChemSupplyAustralia), chloroform (Rowe Scientific) and ethanol (POCD Scientific) were used as received. Tetrachloroauric acid [63], Dec-1-ynide/TOAB stabilised AuNPs [17] and TOAB stabilised AuNPs [56] were prepared using literature procedures. Synthesis of chloro(dimethylsulfide)gold(I) was prepared from a previously published report [64]. All glassware and stir bars were cleaned with Aqua Regia ($HCI:HNO_3$).

TGA measurements were carried out using a TA Instruments SDT Q600 with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere (flow rate of 100 ml min^{-1}). UV-visible spectra were recorded on an Agilent Cary 60 spectrophotometer. Samples were prepared in a quartz cuvette by dissolving ∼ 0.4 mg of AuNP sample in toluene (8 mL). ^1H NMR spectra were recorded using a Bruker NMR spectrometer operating at 400 MHz. Spectra were referenced using residual non-deuterated signals $CDCl_3$ (1H δ 7.26). TEM images were acquired using a JEOL JEM-F200 FE-TEM operating at 200 kV and fitted with a Gatan Rio 1816–4k × 4k camera. TEM samples were prepared by evaporating diluted nanoparticle solutions onto carbon-coated copper grids. The acquired images were analysed using ImageJ software (https://imagej.nih.gov/ij/). SEM was performed at Western Sydney University. A Zeiss Merlin field emission gun scanning electron microscope (FEGSEM) was utilised for imaging samples prepared on stubs. The FEGSEM was operated at 10kV accelerating voltage in Hivac mode at a working distance of ∼3 mm. Secondary and in-lens secondary detectors were both utilised for imaging.

4.2. Synthetic procedures

Synthesis of dec-1-ynide/TOAB-stabilised AuNPs—Method A. Dec-1-ynide/TOAB-stabilised AuNPs was synthesised using a modified literature method [17]. A solution of tetrachloroauric acid (5 mL, 0.027 M, 0.14 mmol) was mixed with TOAB (0.29 g, 0.56 mmol,) in 10 ml of toluene. After 15 min, decyne (3.3 mg, 0.42 mmol) in 5 ml of toluene was added to the solution then cooled. After 15 min a cold, freshly made aqueous solution of $NaBH_4$ (3.5 ml, 1.4 mmol) was added dropwise over 30 s. After further stirring for 12 h, the organic layer was separated and evaporated under a stream of dry nitrogen gas. Acetonitrile was added to the residue to precipitate a black solid. The acetonitrile was removed using a pipette, and the solid was washed with acetonitrile a further five times. ^1H NMR ($CDCl_3$, 400 MHz): 3.36 (8 H, t, J = 8 Hz), 1.72–1.62 (8 H, m), 1.45–1.33 (16 H, m), 1.33–1.19 (24 H, m), 0.88 (12 H, t, J = 7 Hz).

Synthesis of dec-1-ynide/TOAB-stabilised AuNPs—Method B. Dec-1-ynide/TOAB-stabilised AuNPs were using a modified literature method [17]. A solution of tetrachloroauric acid (5 ml, 0.027 M, mmol) was cooled to −10 °C then mixed with TOAB (0.29 g, 0.56 mmol,) in 10 ml of toluene. After 15 min, decyne (0.63 g, 4.5 mmol) in 53 ml of toluene was added to the solution. After 15 min a cold, freshly made aqueous solution of $NaBH_4$ (3.5 ml, 1.4 mmol) was added instantly. After further stirring for 12 h the organic layer was separated and evaporated under a stream of dry nitrogen gas. The acetonitrile was removed using a pipette, and the solid was washed with acetonitrile a further five times. ^1H NMR ($CDCl_3$, 400 MHz): 3.37 (8 H, t, J = 8 Hz), 1.73–1.62 (8 H, m), 1.45–1.34 (16 H, m), 1.34–1.18 (24 H, m), 0.88 (12 H, t, J = 6 Hz).

Synthesis of TOAB-stabilised AuNPS—Method C. TOAB-stabilised AuNPs was synthesised using a modified literature method [56]. A solution of tetrachloroauric acid (6.7 ml, 0.027 M, 0.18 mmol) was mixed with TOAB (0.49 g, 0.9 mmol) in 6 ml of toluene then cooled on ice. After 15 min a cold, freshly made aqueous solution of $NaBH_4$ (0.056 g, 1.5 mmol, 6 ml) was added dropwise over 30 s. After further stirring for 12 h the organic layer was separated and evaporated under N_2 to near dryness then washed with water. ^1H NMR ($CDCl_3$, 400 MHz): 3.35 (8 H, t, J = 8 Hz), 170–1.61 (8 H, m), 1.44–1.33 (16 H, m), 1.33–1.20 (24 H, m), 0.88 (12 H, t, J = 7 Hz).

Synthesis of gold(I)dec-1-ynide. Gold(I) dec-1-ynide was synthesised using a modified literature procedure [34]. Chloro(dimethylsulfide)gold(I) (100 mg, 0.34 mmol) was added to dichloromethane (10.0 mL), decyne (77.4 μl, 0.43 mmol), and triethylamine (60.3 μl, 0.43 mmol) in a 20 mL scintillation vial and stirred in the dark for two hours. The solution was then evaporated under a stream of dry nitrogen gas and the resulting powder washed with water, ethanol, and diethyl ether. Yield: 95 mg (84%). ^{1}H NMR ($CDCl_3$, 400 MHz): 2.62 (2 H, *t*, $J = 7$ Hz), 1.67–1.59 (2 H, quint, $J = 7$ Hz), 1.47–1.38 (2 H, m), 1.33–1.21 (8 H, m), 0.88 (3 H, *t*, $J = 7$ Hz).

Synthesis of dec-1-ynide@AuNPs—Method D. Gold(I) dec-1-ynide (30 mg, 0.090 mmol) was dissolved in toluene (1 ml) and then mixed with TOAB (0.19 g, 0.36 mmol dissolved in 6.5 ml of toluene) then cooled. After 15 min a cold, freshly made aqueous solution of $NaBH_4$ (2.3 ml, 0.90 mmol, 0.4 M) was added instantly. After further stirring for 12 h, the organic layer was separated and concentrated to near dryness under a stream of dry nitrogen gas. The solution was then precipitated in methanol, and washed twice. Yield: 15 mg (52% based on gold). ^{1}H NMR ($CDCl_3$, 400 MHz): 2.62 (2 H, *t*, $J = 7$ Hz), 1.66–1.59 (2 H, quint, $J = 7$ Hz), 1.47–1.37 (2 H, m), 1.33–1.22 (8 H, m), 0.88 (3 H, *t*, $J = 7$ Hz).

Synthesis of dec-1-ynide@AuNPs—Method E. Gold(I)dec-1-ynide (30 mg, 0.090 mmol) in toluene (1 ml) was mixed with TOAB (0.19 g, 0.36 mmol,) in 6.5 mL of toluene. After 15 min a freshly made aqueous solution of $NaBH_4$ (1.2 ml, 0.45 mmol, 0.4 M) was added dropwise over 60 s. After further stirring for 12 h, the organic layer was separated and concentrated to near dryness under a stream of dry nitrogen gas. The solution was then precipitated in acetonitrile, and washed twice. ^{1}H NMR ($CDCl_3$, 400 MHz): 3.31 (8 H, *t*, $J = 8$ Hz), 1.72–1.48 (m), 1.44–1.34 (16 H, m), 1.34–1.21 (24 H, m), 0.88 (12 H, *t*, $J = 7$ Hz).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Acknowledgments

This research is supported by an Australian Government Research Training Program Scholarship. We acknowledge Dr Richard Wuhrer, Dr Laurel George and Dr Daniel Fanna at the Advanced Materials Characterisation Facility (AMCF) of Western Sydney University for access to its instrumentation and staff. We thank microstructural analysis unit (UTS) for assistance with TEM.

Author contributions

Paige K Summers: Investigation, methodology, formal analysis, writing. Andrew M McDonagh: conceptualisation, writing.

Conflict of interest

There are no conflicts to declare.

ORCID iD

Andrew M McDonagh https://orcid.org/0000-0002-9502-1175

References

[1] Daniel M-C and Astruc D 2004 *Chem. Rev.* **104** 293–346
[2] Sardar R, Funston A M, Mulvaney P and Murray R W 2009 *Langmuir* **25** 13840–51
[3] Amendola V, Pilot R, Frasconi M, Marago O M and Iati M A 2017 *J. Phys.* **29** 203002
[4] Kimling J, Maier M, Okenve B, Kotaidis V, Ballot H and Plech A 2006 *J. Phys. Chem. A* **110** 15700–7
[5] Bilal M and Bandyopadhyay S 2025 *Discover Nano* **20** 1–15
[6] Im J *et al* 2025 *Adv. Sci.* **12** 2415496
[7] Abdussalam-Mohammed W, Alshaikh M M, Shah P and Bhattarai A 2025 *Nanoscale Adv.* **7** 3255
[8] Xia M, Li T, Ye Y and Li Y 2025 *Chem. Eng. J.* **508** 161086
[9] Shan J and Tenhu H 2007 *Chem. Commun.* **44** 4580–98
[10] Xia M, Zhou J, Hu L and Li Y 2024 *J. Environ. Chem. Eng.* **12** 113004
[11] Xia M, Ye Y, Li T and Li Y 2025 *Langmuir* **41** 7080–8
[12] Kaur G, Thimes R L, Camden J P and Jenkins D M 2022 *Chem. Commun.* **58** 13188–97
[13] Feng X-K, Chen R, Chen P-Q, Wang G-D, Ren P-C, Guo X-K, Weng Y and Dong X-Y 2025 *Dalton Trans.* **54** 6373–8
[14] Tao J, Zheng D, Tang Y, He H, Zhang Y, Yang Y, Dai L, Zha H, Sang Y and Nie Z 2025 *Angew. Chem.* **137** e202419640
[15] Catalán-Toledo J, Djafari J, Mas-Torrent M and Crivillers N 2024 *Am. Chem. Soc. Appl. Nano Mater.* **7** 5242–51

[16] Liu Y-Q, Chao Y-C, Xu S-Q, Peng Y-R, Syu J-J and Yang X-H 2024 *Am. Chem. Soc. Appl. Mater. Interfaces* **16** 58262–73
[17] Zhang S, Chandra K L and Gorman C B 2007 *J. Am. Chem. Soc.* **129** 4876–7
[18] Lei Z, Li J-J, Wan X-K, Zhang W-H and Wang Q-M 2018 *Angew. Chem., Int. Ed.* **57** 8639–43
[19] Maity P, Takano S, Yamazoe S, Wakabayashi T and Tsukuda T 2013 *J. Am. Chem. Soc.* **135** 9450–7
[20] Maity P, Tsunoyama H, Yamauchi M, Xie S and Tsukuda T 2011 *J. Am. Chem. Soc.* **133** 20123–5
[21] Ma X, Tang Z, Qin L, Peng J, Li L and Chen S 2020 *Nanoscale* **12** 2980–6
[22] Park H, Shin D J and Yu J 2021 *J. Chem. Educ.* **98** 703–9
[23] Kobayashi N, Kamei Y, Shichibu Y and Konishi K 2013 *J. Am. Chem. Soc.* **135** 16078–81
[24] Sugiuchi M, Shichibu Y, Nakanishi T, Hasegawa Y and Konishi K 2015 *Chem. Commun.* **51** 13519–22
[25] Wang Y *et al* 2016 *J. Am. Chem. Soc.* **138** 3278–81
[26] Hoft R, Ford M, García-Suárez V, Lambert C and Cortie M 2007 *J. Phys.* **20** 025207
[27] Tang Q and Jiang D-E 2014 *J. Phys. Chem. C* **119** 10804–10
[28] Hu X, Li P, Xu D, Liu H, Hao Q, Zhang M, Wang Z, Wei T and Dai Z 2024 *J. Am. Chem. Soc.* **146** 32965–78
[29] Weston R P, Chen Y, Dzwonczyk T J, Veras J A, Sevigny A M and Landis E C 2022 *J. Phys. Chem. C* **126** 9673–82
[30] Herrer L, González-Orive A, Marqués-González S, Martín S, Nichols R J, Serrano J L, Low P J and Cea P 2019 *Nanoscale* **11** 7976–85
[31] Yang Z, Pujari S P, Armstrong R, Mathwig K, Rutjes F P J T, Smulders M M J and Zuilhof H 2025 *Langmuir* **41** 6197–207
[32] Du J, Xu H, Zhu X, Long K, Lang J, Jiang L, Xiong E, Liu J and Yang R 2025 *Angew. Chem., Int. Ed.* **64** e202424351
[33] Duan H, Yang T, Sklyar W, Chen B, Chen Y, Hanson L A, Sun S, Lin Y and He J 2024 *Nano Lett.* **24** 5847–54
[34] Hosier C A, Anderson I D and Ackerson C J 2020 *Nanoscale* **12** 6239–42
[35] Ito S, Takano S and Tsukuda T 2019 *J. Phys. Chem. Lett.* **10** 6892–6
[36] Guan Z-J, Hu F, Li J-J, Wen Z-R, Lin Y-M and Wang Q-M 2020 *J. Am. Chem. Soc.* **142** 2995–3001
[37] Brust M, Walker M, Bethell D, Schiffrin D J and Whyman R 1994 *J. Chem. Soc. Chem. Commun.* 801–2
[38] Guan Z-J, Hu F, Li J-J, Liu Z-R and Wang Q-M 2020 *Nanoscale* **12** 13346–50
[39] Wan X-K, Guan Z-J and Wang Q-M 2017 *Angew. Chem., Int. Ed.* **56** 11494–7
[40] Li J-J, Liu Z, Guan Z-J, Han X-S, Shi W-Q and Wang Q-M 2022 *J. Am. Chem. Soc.* **144** 690–4
[41] Wang J-Q, Shi S, He R-L, Yuan S-F, Yang G-Y, Liang G-J and Wang Q-M 2020 *J. Am. Chem. Soc.* **142** 18086–92
[42] Ma X, Ma G, Qin L, Chen G, Chen S and Tang Z 2020 *Sci. China Chem.* **63** 1777–84
[43] Summers P K, Wuhrer R and McDonagh A M 2024 *J. Nanopart. Res.* **26** 97
[44] Summers P K, Angeloski A, Wuhrer R, Cortie M B and McDonagh A M 2023 *Phys. Chem. Chem. Phys.* **25** 7170–5
[45] King S R, Gentle A R, Cortie M B and McDonagh A M 2018 *J. Phys. Chem. C* **122** 12098–105
[46] King S R, Shimmon S, Totonjian D D and McDonagh A M 2017 *J. Phys. Chem. C* **121** 13944–51
[47] King S R, Shimmon S, Gentle A R, Westerhausen M T, Dowd A and McDonagh A M 2016 *Nanotechnology* **27** 215702
[48] Cortie M B, Coutts M J, Ton-That C, Dowd A, Keast V J and McDonagh A M 2013 *J. Phys. Chem. C* **117** 11377–84
[49] Coutts M J, Cortie M B, Ford M J and McDonagh A M 2009 *J. Phys. Chem. C* **113** 1325–8
[50] Singh R 2019 *3 Biotech* **9** 415
[51] Chang J, Zhang A, Huang Z, Chen Y, Zhang Q and Cui D 2019 *Talanta* **198** 45–54
[52] Ozcicek I, Aysit N, Cakici C and Aydeger A 2021 *Mater. Sci. Eng. C* **128** 112308
[53] Bano A, Dawood A, Saira F, Malik A, Alkholief M, Ahmad H, Khan M A, Ahmad Z and Bazighifan O 2023 *Sci. Rep.* **13** 12359
[54] Leff D V, Ohara P C, Heath J R and Gelbart W M 1995 *J. Phys. Chem.* **99** 7036–41
[55] Hostetler M J *et al* 1998 *Langmuir* **14** 17–30
[56] Wang Y Q, Liang W S and Geng C Y 2009 *Nanoscale Res. Lett.* **4** 684
[57] Yu C, Zhu L, Zhang R, Wang X, Guo C, Sun P and Xue G 2014 *J. Phys. Chem. C* **118** 10434–40
[58] Casado R, Contel M, Laguna M, Romero P and Sanz S 2003 *J. Am. Chem. Soc.* **125** 11925–35
[59] Badia A, Gao W, Singh S, Demers L, Cuccia L and Reven L 1996 *Langmuir* **12** 1262–9
[60] Terrill R H, Postlethwaite T A, Chen C-H, Poon C-D, Terzis A, Chen A, Hutchison J E, Clark M R and Wignall G 1995 *J. Am. Chem. Soc.* **117** 12537–48
[61] Thomas S R, Yang W, Morgan D J, Davies T E, Li J J, Fischer R A, Huang J, Dimitratos N and Casini A 2022 *Chem. Eur. J.* **28** e202201575
[62] MacLeod M J and Johnson J A 2015 *J. Am. Chem. Soc.* **137** 7974–7
[63] King S R, Massicot J and McDonagh A 2015 *Metals* **5** 1454–61
[64] Uson R, Laguna A, Laguna M, Briggs D A, Murray H H and Fackler J P Jr 1989 *(Tetrahydrothiophene)gold(I) or Gold(III) Complexes* ed H D Kaesz (*Inorganic Syntheses*) (Wiley)