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RESEARCH PAPER

Investigation of the role of $NaBH_4$ in the chemical synthesis of gold nanorods

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Abstract An improvement in the previously reported seed-mediated chemical synthesis of gold nanorods (GNRs) is reported. Monodisperse GNRs have been synthesized in a one-step protocol. The addition of controlled quantity of sodium borohydride ($NaBH_4$) directly into the growth solution produced uniform GNRs, formed by in situ nucleation and growth. In order to arrive at the conclusion, we studied the formation of GNRs with various seeds, of metals of widely differing crystal structures, and there were no variations in the properties of the GNRs formed. The role of $NaBH_4$ in the growth of GNR, which has not been covered in previous reports, is discussed in detail. The dependence of longitudinal plasmon peak on the concentration of $NaBH_4$ is compared with the dependence of residual concentration of $NaBH_4$ in the seed solution, which is added to the growth solution in seed-mediated synthesis. The study shows that $NaBH_4$ plays an important role in the formation of GNRs. This proposed protocol offers a number of advantages: one-step preparation of GNRs, significant reduction in the preparation time to 10 min, high monodispersity of GNRs, and tailorability of the aspect ratio depending on $NaBH_4$ concentration. It is suggested that $NaBH_4$ added to the growth solution leads to in situ formation of the seed particles of the size of 3–5 nm which enables the growth of GNRs. The growth of GNRs suggested here is likely to have an impact on the preparation of other anisotropic structures. Our single-pot methodology makes the procedure directly adaptable for commercial-scale production of GNRs and for their synthesis even in undergraduate laboratories.

Keywords Gold nanorods · Seed particles · Growth solution · Metals · Sodium borohydride · Nanoparticles

Introduction

Anisotropic metal nanostructures such as nanorods (Murphy et al. 2005; Perez-Juste et al. 2005), prisms or triangles (Millstone et al. 2005; Sajanlal and Pradeep 2008; Ah et al. 2005; Jin et al. 2001), wires (Hu et al. 1999; Wiley et al. 2005), multipods (Hao et al. 2004), stars (Nehl et al. 2006), tadpoles (Hu et al. 2004), and a variety of other structures are subjects of intense investigation currently. Crystals formed with spherical nanoparticles, so called superlattices, are often anisotropic and show interesting properties (Nishida et al. 2008; Yang et al. 2006).

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GNRs belong to an important class of anisotropic nanostructures exhibiting very strong correlation between optical properties and aspect ratio (Murphy et al. 2005; Perez-Juste et al. 2005). Their photophysical properties have triggered a huge interest in designing novel applications in medical diagnostics and therapeutics (Tong et al. 2007), sensors (Rex et al. 2006), surface enhanced Raman scattering (Nikoobakht and El-Sayed 2003b), and optical waveguides (Maier et al. 2003). Recently, macroscopically aligned nanorod arrays were reported, bringing them a step closer toward the fabrication of waveguides and nano-gratings (Sreeprasad et al. 2008). Most of the applications envisaged require precise control over the aspect ratio and size distribution. In this respect, several synthetic protocols have been reported; principal among them are template assisted (Van der Zande et al. 1997), electrochemical (Yu et al. 1997), photochemical (Kim et al. 2002), and seed-mediated (Jana et al. 2001a, b) chemical syntheses. Seed-mediated synthesis has been a subject of intensive research interest owing to its reliability in the preparation of GNRs with higher yields (Sau and Murphy 2004). Synthesis using ~4 nm gold nanoparticle seeds have been used for the growth of GNRs. The size, protecting agent, and the concentration of the seed are most important factors for the control of the aspect ratio of nanorods (Gole and Murphy 2004). Thus, commonly followed chemical synthesis of GNRs is a two-pot strategy: synthesis of gold seeds and their subsequent addition to the growth solution (Sau and Murphy 2004). Important role of seeds in GNR formation has been reiterated by anchoring them on a substrate and growing GNRs by dipping the immobilized seeds in the growth solution (Taub et al. 2003; Wei et al. 2004). A recent report suggests the formation of GNRs through the use of silver seeds (Xu et al. 2007).

In this study, the importance of $NaBH_4$ in the growth of GNRs is reported. We find that gold seeds can be grown in situ in the growth solution by controlling the concentration of $NaBH_4$, which leads to one-step formation of GNRs. Highly uniform GNRs can be formed in a single step by controlling the concentration of $NaBH_4$ and thus the process does not require the external addition of any metal seed into the growth solution. The nanorods synthesized are chemically, structurally, and spectroscopically similar to those obtained from the seed-mediated approach and are highly uniform, so that a purification step can be avoided for a large-volume synthesis. In order to reach this conclusion, GNRs were formed starting from various seeds, derived from metals of widely different crystal structures. All formed similar GNRs in terms of structural and spectroscopic properties. The similarity of GNRs in these experiments suggested the possibility of forming seeds in situ, which subsequently aided the growth of nanorods. Based on the results from the experiment, it is concluded that $NaBH_4$ present in the pre-formed seeds helps in the GNR growth. Several other control experiments were also done. The complete destruction of active BH_4^- in the preformed seeds makes the GNR growth impossible, while addition of measured quantity of BH_4^- in the growth solution itself facilitates GNR growth. Conclusions from this study in the context of the existing knowledge allow us to come up with a complete picture for the growth of GNRs.

Experimental section

Materials

Cetyltrimethylammonium bromide (CTAB) was purchased from SD Fine Chemicals, India. Tetrachloroauric acid trihydrate ($HAuCl_4{\cdot}3H_2O$) and silver nitrate ($AgNO_3$) were purchased from CDH, India. Ascorbic acid (AA) was purchased from Hi-Media Chemicals, India. $NaBH_4$ was purchased from Sigma-Aldrich, USA. All chemicals were used without further purification. Triply distilled water was used throughout the experiments.

Synthesis of GNRs using metal seeds

The growth solution was prepared based on a modified literature procedure reported earlier by Sau and Murphy (2004), but the procedure was slightly modified. We studied the formation of GNRs with a variety of metal seeds, chosen on the basis of differing lattice structures in the bulk and ease of synthesis. We used Fe (bcc), Ru, and Cd (hcp), Cu, Pb, Ag, and Au (ccp), Hg (rhombohedral), In (tetragonal), and Sb (trigonal). The seeds were prepared from their salts by the reduction of $NaBH_4$. For example, the Pb seed particles were prepared by adding 100 μL of 10 mM ice-cold $NaBH_4$ to 500 µL of 10 ppm $Pb(NO_3)_2$ solution. The solution prepared was colorless upon visual observation. From the TEM measurements, the size of the Pb seed particles was found to be 3–5 nm. A total of 50 µL of the Pb seed particles was added to the growth solution containing 5 mL of 100 mM CTAB, 250 µL of 10 mM $HAuCl_4 \cdot 3H_2O$, 32.5 µL of 10 mM $AgNO_3$, and 35 µL of 100 mM AA. The solution was kept undisturbed for 3 h for the complete growth of nanorods. The solution was centrifuged at 11,000 rpm for 20 min to remove excess CTAB and other ions. The pellet was redispersed in triply distilled deionized water. The other metal seeds were prepared in similar ways. The different seed particles were added separately to the growth solution and kept undisturbed for 3 h for the growth of GNRs. Several of the metal seeds, prepared from metals such as Fe, Cu etc. are expected to be highly reactive in water and therefore the seed solutions were used immediately after preparation. The stability, chemical composition, and structure of these seed particles were not investigated.

Synthesis of GNRs using $NaBH_4$

For a typical synthesis, 1.67 mM of $NaBH_4$ was prepared in ice-cold water. A growth solution as mentioned above was prepared. A total of 50 µL of freshly prepared ice-cold $NaBH_4$ was added to the growth solution. The growth of nanorods was observable within a few minutes of the addition of $NaBH_4$ and no apparent change was seen after 10 min. However, the mixture was kept undisturbed at room temperature for 3 h to complete the growth of nanorods. The nanorod solution was centrifuged twice at 11,000 rpm for 20 min to remove excess CTAB and other ions. The pellet was redispersed in triply distilled deionized water.

Instruments

Ultra violet–visible absorption spectra were recorded using Perkin-Elmer Lambda 25 spectrophotometer. High resolution transmission electron microscopy (HRTEM) and Energy dispersive X-ray analysis (EDAX) were carried out with an Oxford EDAX housed in JEOL 3010, 300 kV instrument equipped with a UHR polepiece. The samples were prepared by dropping the dispersion on carbon coated copper grids.

Results and discussion

Formation of GNRs using different metal seeds

Seed particles of elements, such as Fe, Ru, Cd, Cu, Pb, Ag, Au, Hg, In, and Sb, were prepared by the reduction of $NaBH_4$. Metal salts were used as precursors for the seed growth. Figure 1A shows a transmission electron microscopic (TEM) image of Pb seed particles and Fig. 1B shows the lattice resolved image of a single particle in high resolution. From the TEM measurements, we found that the size of the seed particles was 3–5 nm. The seed particles upon addition to the growth solution gave GNRs. The nucleation was initiated upon the addition of 50 µL suspension of the seed particles to the above growth solution. All the seed particles successfully formed

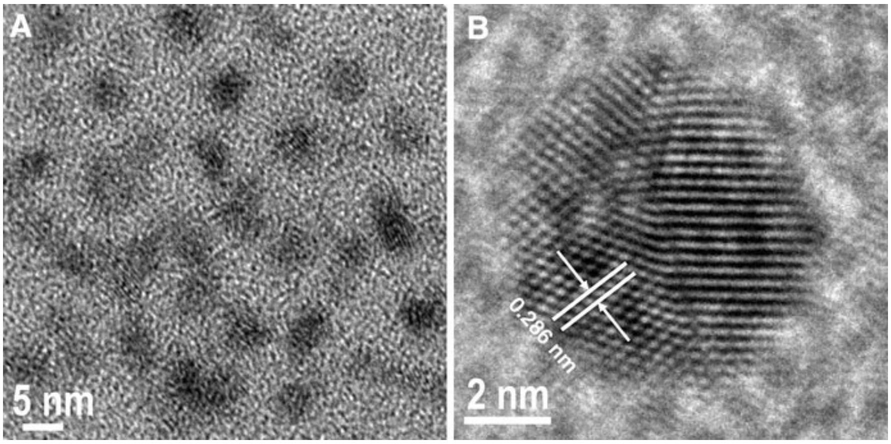


Fig. 1 **A** TEM image of Pb seed particles and **B** HRTEM image of a Pb seed particle

GNRs. A typical large area TEM image of the GNRs formed is shown in Fig. S1 (Supporting Information). The aspect ratio of GNRs formed was 3.4 (diameter 11 nm).

The GNRs formed are of well-defined structure, although the precursor metals have different crystal structures. All the products were thoroughly investigated by absorption spectroscopy and TEM. Under the same reaction conditions, all the metal seeds formed GNRs of almost the same aspect ratio. The longitudinal surface plasmon (LSP) of the nanorods was observed in between 770 and 810 nm, while the transverse plasmon (TSP) was almost the same for all. The absorption spectra of GNRs synthesized using different metal seeds are given in Fig. 2A. A typical high-resolution TEM image of GNRs formed using Pb seed is given in Fig. 2B. The lattice structure of GNR is observed to be fcc irrespective of the differing crystal structure of the metals used to grow the GNRs. HRTEM images of GNRs synthesized using different metal seeds were examined to see the presence of other crystal structures in them. Figure 3 shows the HRTEM of GNRs exhibiting fcc crystal structure, formed using different seed particles. The entire structure of the rods, starting from the tip, was examined in each case and the nanorods as a whole were found to be single crystals. The concentration of the metal ions used in the seed solution is very less (10 ppm) as compared to $NaBH_4$. As a result of all these observations, we thought that something else in the medium is nucleating the GNR growth. From several control experiments as described below, we concluded that the excess $NaBH_4$ present in the seed solution leads to in situ formation of gold seed in the growth solution which aids in the one-step formation of GNRs.

In situ synthesis of GNRs using $NaBH_4$

In order to ensure whether $NaBH_4$ alone was able to form GNRs, 50 μL of 1.67 mM ice-cold $NaBH_4$ was added directly to ~5 mL of the growth solution. UV–visible absorption spectroscopy carried out in a time-dependent manner during the reaction showed the simultaneous appearance and subsequent saturation of the TSP and LSP at 511 and 796 nm, respectively, within 10 min of addition of $NaBH_4$. This indicates the formation of GNRs (Fig. 4A). The formation of GNRs was checked at every stage by absorption spectroscopy and TEM. There is an insignificant shift in TSP after 10 min indicating that nanorod growth is complete, although the reaction mixture was kept undisturbed for 3 h. This product was centrifuged at 11,000 rpm for 20 min in order to remove excess CTAB and unreacted ions. The residue was redispersed in triply distilled deionized

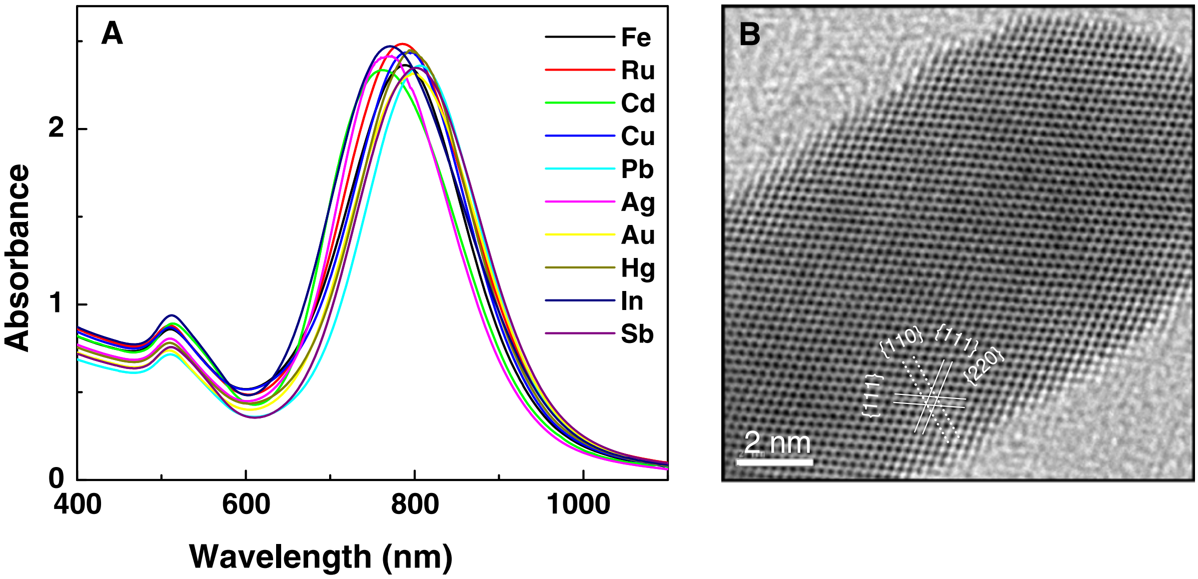


Fig. 2 **A** UV–visible spectra of GNRs formed using various metal seeds. **B** HRTEM of one end of a GNR formed from Pb seeds showing its fcc crystal structure

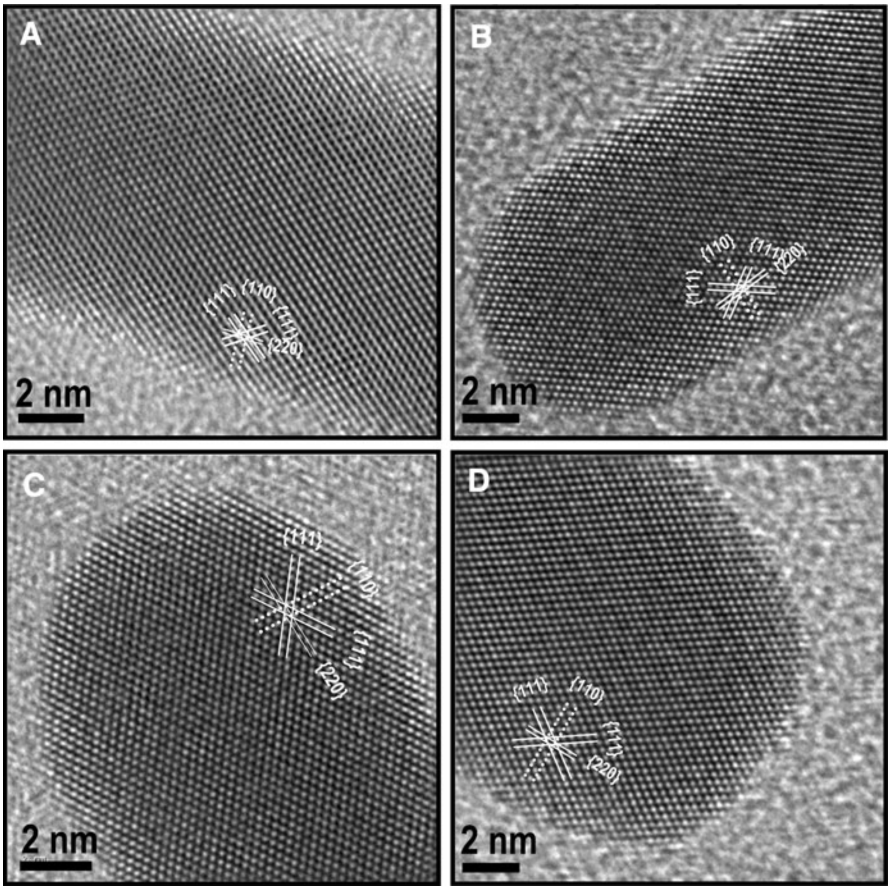


Fig. 3 HRTEM images of nanorods formed using different seed particles: (**A**) Fe (*bcc*), (**B**) Cd (*hcp*), (**C**) Sb (*trigonal*), and (**D**) In (*tetragonal*). Although the metals are of different crystal structures, the GNRs formed are fcc

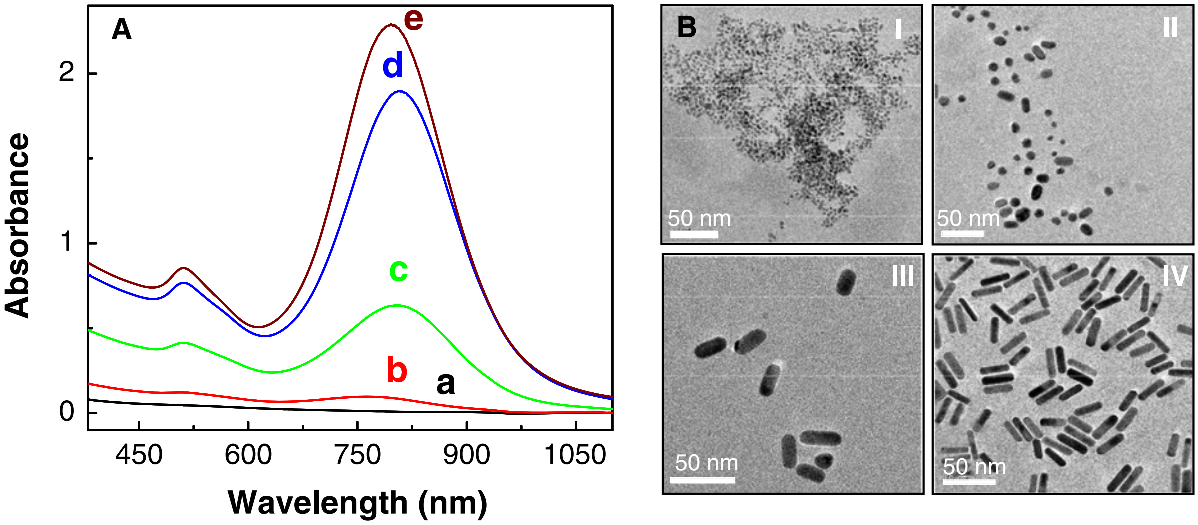


Fig. 4 **A** UV–visible spectra of GNRs obtained at different time intervals after adding $NaBH_4$ solution: *a* 0, *b* 3, *c* 5, *d* 8, and *e* 10 min. **B** TEM images of nanorods formed at different stages after adding $NaBH_4$ solution: (I) 3, (II) 5, (III) 8, and (IV) 10 min. Although absorption spectrum does not change significantly after 10 min, the number of spherical particles reduces almost to zero upon keeping the reaction mixture for 3 h

water. TEM images of the redispersed material showed the presence of GNRs with good monodispersity. No spherical particles were observed. The resulting GNRs have an aspect ratio of 3.4 with a diameter of 11 nm. Figure 4B shows the TEM images of nanorods formed at different stages after the addition of $NaBH_4$. The HRTEM of the GNRs was similar to that as given in Fig. 2B.

The aspect ratio can be tuned by varying the volume of $NaBH_4$ solution added to the growth solution (Fig. 5). It was observed that the aspect ratio decreased with increase in the volume of $NaBH_4$ used, finally resulting in spherical nanoparticles (aspect ratio, 1) at 0.5 mL (keeping all other parameters the same). Under optimum conditions, GNRs formed the aspect ratio of 3.4, by the addition of 50 μL of 1.67 mM $NaBH_4$ (trace a). With further increase in the amount of $NaBH_4$ (500 μL of 1.67 mM $NaBH_4$), the LSP merged with the TSP and a single absorption peak was obtained, characteristic of spherical particles (trace e). A similar observation was found in the previous seed-mediated synthesis which showed that aspect ratio of GNRs decreased with increasing the amount of gold seeds (Jana et al. 2001a, b; Gole and Murphy 2004). Higher concentration of $NaBH_4$ in the growth solution modified the growth kinetics resulting in the formation of spherical particles.

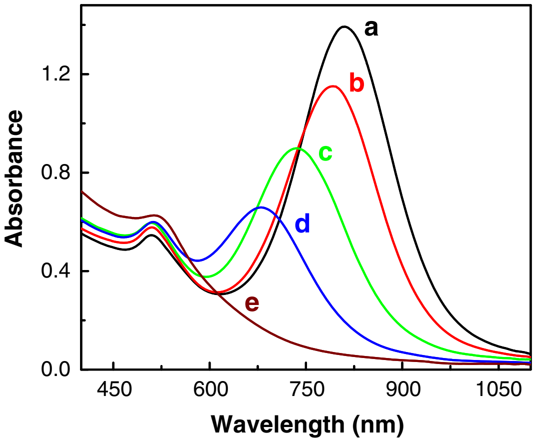


Fig. 5 UV–visible spectra of GNRs formed with increasing amount of $NaBH_4$: *a* 50 μL, *b* 100 μL, *c* 200 μL, *d* 300 μL, and *e* 500 μL

Influence of different parameters of the growth solution on GNR growth

Further, the effect of concentration of other reactants, namely, Au^{3+}, Ag^{+}, and CTAB were monitored carefully. Variation of the Au^{3+} concentration in the growth solution alters the aspect ratio of the nanorods. A total of 250 μL of 10 mM Au^{3+} yielded well-defined nanorods (aspect ratio, 3.4). Increase in the concentration of Au^{3+} in the growth solution leads to redshift of the LSP which indicates that higher aspect ratio GNRs could be formed. Similar results were reported by Murphy's group (Sau and Murphy 2004). But beyond certain concentration of Au^{3+}, no nanorods were formed. For example, an addition of 500 μL of 10 mM Au^{3+} formed no nanorods. This was confirmed by both UV–visible (Fig. 6A) and TEM. We suspected that AA was not enough to reduce all the Au^{3+} ions present in the growth solution. Upon the addition of 35 μL of AA to the solution containing 500 μL of 10 mM Au^{3+}, nanorods were formed, confirming the suggestion (Fig. 6A, trace h). The initial reduction of Au^{3+} to Au^{1+} was noticeable by the color change (yellow to colorless), but there was no complete color change when larger amounts of Au^{3+} ions were present.

Earlier reports relied on Ag^{+} for achieving GNRs of desired aspect ratio (Kim et al. 2002; Nikoobakht and El-Sayed 2003a). The role of Ag^{+} was more noticeable in the formation of short GNRs in high yields (Jana et al. 2001a, b). In this protocol, no GNRs were formed in the absence of $AgNO_3$. The UV–visible spectrum showed only one absorption at 536 nm, attributable to non-rod shaped particles. The absorption spectrum of the solution in the absence of $AgNO_3$ is shown in Fig. S2.

Variation of the concentration of AA alters the aspect ratio of GNRs. Shorter GNRs were observed with an increase in the concentration of AA, keeping all the other parameters constant. Similar observations were made previously (Sau and Murphy 2004). The GNRs did not form below a certain concentration of AA, due to incomplete reduction of Au^{3+} to Au^{1+}. It was also observable in the color (due to Au^{3+}) of the growth solution. Below 20 μL of 100 mM of AA, no nanorods were formed. Spectral data showed that the addition of 35 μL of 100 mM of AA gives better GNRs. The absorption features of different concentrations of AA are shown in Fig. 6B. Different

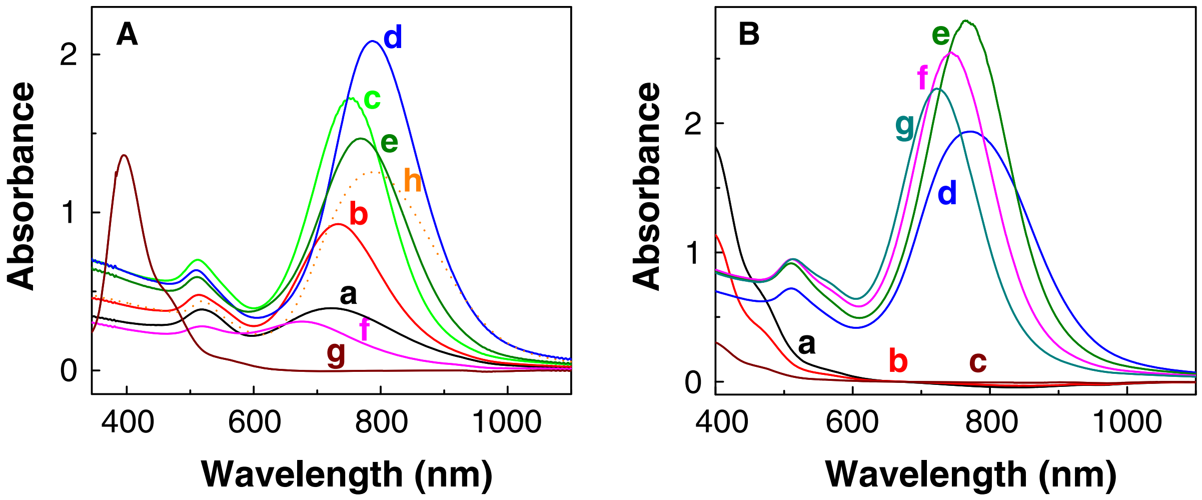


Fig. 6 UV–visible spectra of GNRs prepared using different amount of **A** Au^{3+} ions [*a* 50 µL, *b* 100 µL, *c* 200 µL, *d* 250 µL, *e* 300 µL, *f* 400 µL, *g* 500 µL, and *h* when 35 µL more AA was added to existing (*g*) solution], and **B** AA [*a* 00 µL, *b* 10 µL, *c* 20 µL, *d* 30 µL, *e* 35 µL, *f* 50 µL, and *g* 75 µL]. Concentrations of the solutions used are the same as given in the text

concentrations of CTAB above the critical micellar concentration (CMC) did not make any visible change in the absorption spectrum.

Influence of $NaBH_4$ on non-nucleating seeds

From these studies, the importance in $NaBH_4$ in the formation of in situ seeds may be suggested. In order to confirm this, freshly prepared $NaBH_4$, aged $NaBH_4$ (kept for more than 8 h at room temperature), and heated $NaBH_4$ were used in the synthesis. Freshly prepared $NaBH_4$ formed GNRs, whereas the addition of aged $NaBH_4$ did not result in GNRs. However, $NaBH_4$ preserved at 0 °C, even for 12 h before adding to the growth solution, formed nanorods. In a separate experiment, $NaBH_4$ was heated for 5 min at 100 °C and cooled to room temperature (to ensure complete loss of its reducing action). This did not form nanorods as expected. UV–visible spectra of GNRs grown using aged, boiled, and freshly prepared $NaBH_4$ are shown in Fig. 7. The addition of freshly prepared $NaBH_4$ to either aged or boiled $NaBH_4$ regained their capacity to form nanorods (Fig. 8A, B). These experiments reiterate the vital role of $NaBH_4$ in the formation of GNRs. Through these studies, it is seen that controlled reduction of growth solution is the sole criterion for the formation of GNRs and seeds can be nucleated in situ.

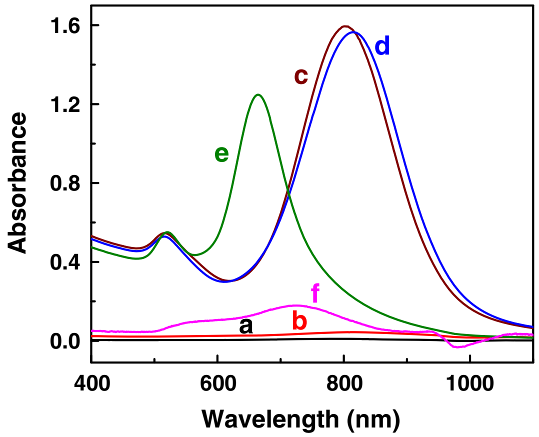


Fig. 7 Absorption spectra of GNRs synthesized with *a* aged $NaBH_4$, *b* heated and cooled $NaBH_4$, *c* freshly prepared $NaBH_4$, *d* fresh Au seed, *e* Au seed at 1 h, and *f* 4 h after preparation

In order to confirm the active role of $NaBH_4$, we tried a few other control experiments as well. Gold colloids of 4 and 16 nm in diameter were used as seed particles. Four nanometer gold colloid was synthesized by the reduction of $NaBH_4$, and 16 nm colloid was synthesized by the reduction of trisodium citrate (Turkevich et al. 1951; Obare et al. 2002). Colloid prepared by the reduction of $NaBH_4$ formed nanorods. Aged 4 nm colloids, where no active BH_4^- is present, could not nucleate nanorods. The colloids

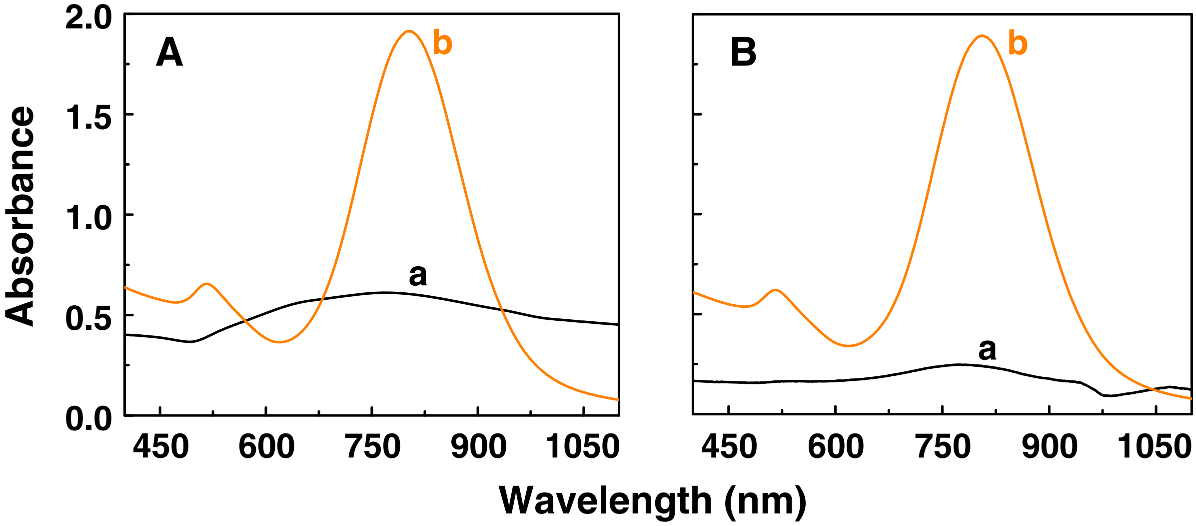


Fig. 8 UV–visible spectra of GNRs prepared by using (**A**) *a* 50 µL of aged $NaBH_4$ (kept for more than 8 h at room temperature) and *b* freshly prepared 50 µL $NaBH_4$ added to aged $NaBH_4$, and (**B**) *a* 50 µL of heated and cooled $NaBH_4$ and *b* freshly prepared 50 µL $NaBH_4$ added to heated and cooled $NaBH_4$

prepared by the reduction of trisodium citrate did not form nanorods at all. However, when $NaBH_4$ was added to citrate colloid and the mixture was added to the growth solution, nanorods were formed (Fig. S3). This provided conclusive evidence that the growth of nanorods was controlled by $NaBH_4$ and that externally synthesized seed particles are not necessary in the nanorod growth.

The effect of $NaBH_4$ concentration on the position of LSP was evaluated. The results for $NaBH_4$ nucleated GNRs were shown in Fig. 5. The changes in the position of LSP with the amount of external seed used (growth performed as per the seed-mediated method) are presented in Fig. S4. An approximate estimate of residual $NaBH_4$ available in the volume of seed solution added to the growth solution is calculated. This can be done by using the fact that one mole of BH_4^- can reduce eight moles of Au^{1+} existing in the growth solution. The data are shown in Fig. S5. The results show that in all the cases of GNR formation, $NaBH_4$ is always present in a limited quantity. The LSP position from these two growth processes is plotted in Fig. 9, as a function of effective BH_4^- available in the growth solution. The data suggest that the GNRs formed by the two methods are quite similar. This is because the effective concentrations of BH_4^- are similar in both the cases as well as other parameters. Note that the residual concentration of $NaBH_4$ in seed-mediated method is likely to be less than the theoretical value as seed solution is left for 2 h, which explains the slight differences between the two cases. It is also important to note that GNR formation happens only when the effective concentration of $NaBH_4$ is significantly less than the concentration of Au^{1+} in the solution. It can be concluded from the figure that $NaBH_4$ is sufficient to induce the formation of GNR.

The original two-step seed-mediated chemical synthesis approach is suggested to study as follows: single

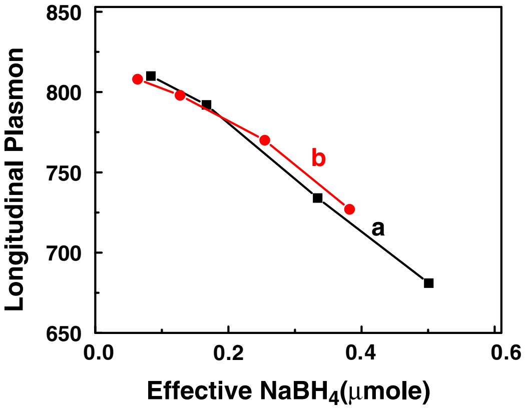


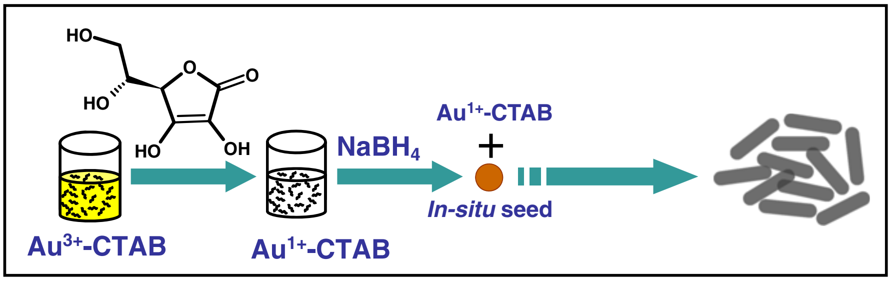
Fig. 9 LSP versus effective $NaBH_4$ concentration in the whole growth solution, *a* $NaBH_4$-based synthesis (*filled square*), and *b* seed-based synthesis (*filled circle*)

crystalline seed particles synthesized externally through the use of $NaBH_4$ as a reducing agent and CTAB as the protecting agent act as nucleation centers during the reaction in the growth solution. Au^{1+} species, present in the growth solution due to the reduction of Au^{3+} using AA, reduces to $Au^{(0)}$ on the seed surface leading to symmetry breaking and the growth of specific facets. During this process of crystal growth, surfactants and silver bromide preferentially binding to the [100] crystal facet, inhibiting the nucleation of $Au^{(0)}$ on the [100] facet, and allowing the growth on stable [111] facet preferentially. The role of various species contributing to the growth of GNR has been summarized earlier (Murphy et al. 2005; Perez-Juste et al. 2005). The formation of $Au^{(0)}$ initiates the process of in situ spherical seed formation in the solution. This is clearly evident from the TEM images taken at different time intervals after the addition of $NaBH_4$. After the formation of seed particles, as reported earlier, certain facets of the seed particles are selectively blocked for further growth due to the action of CTAB and/or silver bromide. During this process of selective facet blocking and nucleation of gold on un-blocked surface, a bilayer micelle of CTAB continues to develop on the longitudinal growth direction. Scheme 1 illustrates the AA-induced reduction of Au^{3+}–CTAB complex to Au^{1+}–CTAB complex in the growth solution. The growth of GNRs initiates with the growth of in situ formed seed particles. The role of AA, $AgNO_3$, and CTAB, as suggested in earlier reports, is observed in this experiment (Murphy et al. 2005; Perez-Juste et al. 2005).

The role of externally added metal seed to the growth of GNR is likely to be minimal based on the findings from this study. If metal seeds were to act as the center for nucleation, traces of such metals should be found in the fully grown GNRs. HRTEM images of the GNR revealed the fcc nature of the NR crystals. An elemental analysis using TEM EDAX confirms the absence of other metals in the GNRs (Fig. S6), implying that the absence of externally added metal seeds in GNRs. Although detection limit of an elemental analysis at these concentrations pose questions, it is difficult to believe that the seeds of varying structures have any effect both in composition and in structure. Note that we used externally added seeds of different metals, with varying crystal structures (e.g., metals used are: Hg (rhombohedral), In (tetragonal), Sb (trigonal), etc.). An earlier reported study on silver seed-based synthesis of GNR revealed the absence of silver in the fully grown GNR (Xu et al. 2007). All of these suggest the in situ formation of gold seeds and thus, $NaBH_4$ plays a critical role in the formation of GNRs. It is also important to highlight the fact that increasing concentration of $NaBH_4$ leads to a blue-shift in the longitudinal plasmon of GNR. This happens because, as the concentration of the reducing agent increases, a large number of in situ seeds are formed in the solution, which are supposedly acting as self-nucleation centers. In turn, the amount of Au^{1+} available for reduction and nucleation on the seed surface reduces drastically, thus the growth of seed to GNR is inhibited, resulting in the formation of spherical particles.

Conclusions

We report a simple one-pot approach for the synthesis of highly uniform GNRs. This method throws important light into the kinetics and nucleation of GNRs. $NaBH_4$ as a controlled reducing agent is found to be vital for the formation of GNRs when compared to the role of externally prepared metal seeds. From various experiments, we conclude that gold seeds can be nucleated in situ by the action of $NaBH_4$ in the growth solution. The method reported is



Scheme 1 Representation of the growth of GNRs using in situ synthesized seed particles

comparatively simple, less time consuming, and may be used even in undergraduate laboratories as well as for the large-scale synthesis of GNRs.

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