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# Chinese Chemical Letters

Original article

# Solvent effect on the synthesis of monodisperse amine-capped Au nanoparticles

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ABSTRACT

A remarkable solvent effect in a single-phase synthesis of monodisperse amine-capped Au nanoparticles is demonstrated. Oleylamine-capped Au nanoparticles were prepared *via* the reduction of $HAuCl_4$ by an amine-borane complex in the presence of oleylamine in an organic solvent. When linear or planar hydrocarbon (*e.g.*, *n*-hexane, *n*-octane, 1-octadecylene, benzene, and toluene) was used as the solvent, high-quality monodisperse Au nanoparticles with tunable sizes were obtained. However, Au nanoparticles with poor size dispersity were obtained when tetralin, chloroform or cyclohexane was used as the solvent. The revealed solvent effect allows the controlled synthesis of monodisperse Au nanoparticles with tunable size of 3–10 nm.

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## 1. Introduction

Colloidal Au nanoparticles have attracted considerable interest due to their potential applications in biolabeling, photonics, catalysis, and so on [1–3]. Sub-10 nm Au nanoparticles with a narrow size distribution can be used to precisely evaluate the size effect or support effect in catalysis [4–7], as well as further serve as building blocks for the construction of high-ordered superlattices or nanostructures [8–12]. Since the development of the Brust–Schiffrin two-phase synthetic method [13], the wet synthesis of monodisperse Au nanoparticles with size less than 10 nm has attracted much research effort and thus received significant progress during the past two decades [1,14–20].

In the developed methods, the use of organic capping agents (*e.g.*, thiol and amine) is generally required to stabilize and facilitate the synthesis of sub-10 nm Au nanoparticles in solutions [13–19]. However, many studies have revealed the synthesis of monodisperse Au nanoparticles highly depends on various factors which at least include capping agent, reducing agent, solvent and temperature [15–18,21–23]. In some cases, a little change of some parameters could result in a great change in the size and quality of the obtained Au nanoparticles [18], making the synthesis hardly repeatable among different groups. Consequently, systematic studies on how reaction parameters influence the formation of Au nanoparticles are essential to develop a highly repeatable synthetic method of high-quality Au nanoparticles.

We now report here a remarkable solvent effect in the synthesis of oleylamine (OAm)-capped Au nanoparticles using a facile one-phase synthesis method. In the synthesis, $HAuCl_4$ was reduced by an amine-borane complex in the presence of OAm in an organic solvent. High-quality monodisperse Au nanoparticles with tunable sizes were obtained when a solvent of linear or planar hydrocarbon (*e.g.*, *n*-hexane, *n*-octane, 1-octadecylene, benzene, toluene) was used. In contrast, the use of solvents, such as tetralin, chloroform and cyclohexane, led to the formation of Au nanoparticles with poor size dispersity. The revealed solvent effect can be used to control the particle size of Au nanoparticles, making it possible to obtain highly monodisperse amine-capped Au nanoparticles with size ranging from 3 nm to 10 nm.

## 2. Experimental

### 2.1. One-step one-phase synthesis of Au nanoparticles

In a typical synthesis of $(5.3 \pm 0.5)$ nm Au nanoparticles, an orange precursor solution of *n*-hexane (10 mL), OAm (10 mL), and $HAuCl_4 \cdot 4H_2O$ (0.25 mmol) was prepared in air and magnetically stirred in 15 °C thermostatic bath under $N_2$ flow ($\sim$30 mL/min) for 10 min. A reducing solution containing 0.25 mmol of TBAB (*tert*-butylamine-borane complex), *n*-hexane (1 mL), and OAm (1 mL) was mixed by sonication and injected into the precursor solution. The reduction was instantaneously initiated and the solution changed to a deep purple color within 5 s. The mixture was allowed to react at 15 °C for 1 h before ethanol (60 mL) was added to precipitate the Au NPs. The Au NPs were collected by centrifugation (6000 rpm, 5 min), washed with ethanol and redispersed in hexane ($\sim$5 mg/mL).

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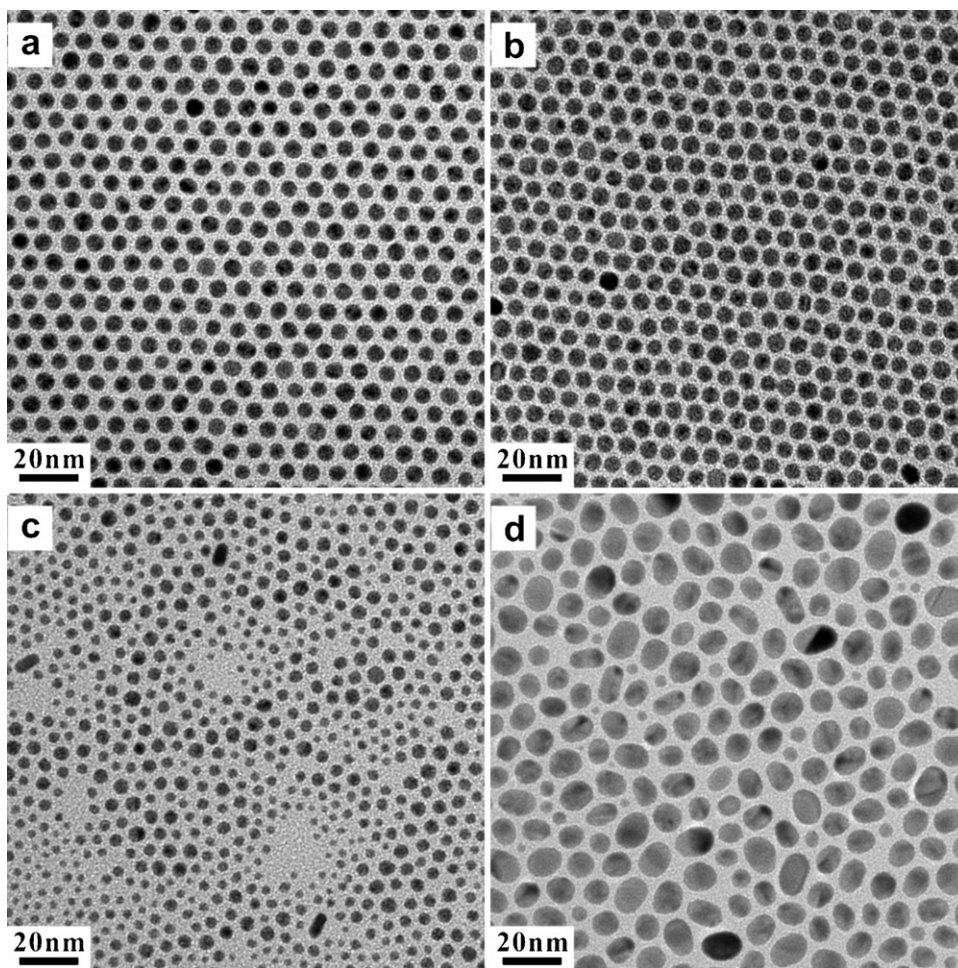
**Fig. 1.** TEM images of Au nanoparticles obtained in equal volume of OAm and (a) *n*-hexane, (b) *n*-octane, (c) tetralin, or (d) chloroform. The average size is $(5.3 \pm 0.5)$ nm, $(5.6 \pm 0.4)$ nm, $(4.2 \pm 0.9)$ nm, and $(7.3 \pm 1.8)$ nm, respectively. Reaction conditions: 0.25 mmol HAuCl$_4$·4H$_2$O, 11 mL OAm, 11 mL selective solvent, 0.25 mmol TBAB, N$_2$ flow, 15 °C, 1 h.

To make sure all the Au(III) precursor was reduced into Au(0), the feed of TBAB should be more than half of Au(III) precursor in mole ratio, which can be calculated as follows:

$$2HAuCl_4 + C_4H_9NH_2 \cdot BH_3 + 3H_2O$$
$$= 2Au(0) + C_4H_9NH_2 + 8HCl + H_3BO_3$$
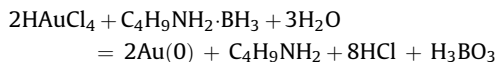
The size of Au nanoparticles was controlled by tuning the ratio of TBAB:HAuCl$_4$·4H$_2$O. All syntheses yielded Au nanoparticles in nearly quantitative yield, since the upper solution after Au precipitation was colorless and there was no color change if some TBAB was introduced into the upper solution.

### 2.2. Seeded growth of 7.7 nm Au nanoparticles

HAuCl$_4$·4H$_2$O (0.0625 mmol, ~25 mg) was dissolved in 5 mL of 1-octadecene (or tetralin) in the presence of 0.5 mL of oleylamine by magnetic stirring. Under the protection of nitrogen, 0.2 mL of $(7.7 \pm 0.5)$ nm Au nanoparticles (5 mg/mL) dispersed in hexane was added into the solution at 60 °C. Au overgrowth was carried out at this temperature for 5 h. After the mixture was cooled to room temperature, 20 mL of isopropyl alcohol was added to the reaction mixture to precipitate the nanoparticles and the product was collected *via* centrifugation (12,000 rpm, 5 min).

### 3. Results and discussion

In this study, the syntheses of Au nanoparticles were carried out under a N$_2$ flow. In a typical synthesis, HAuCl$_4$·4H$_2$O was mixed with OAm in a selective organic solvent (*i.e.*, *n*-hexane, *n*-octane, 1-octadecylene, benzene, toluene, tetralin, chloroform, cyclohexane) to give a homogeneous precursor solution. TBAB, a mild reducing agent [17,18], was dissolved in the selective solvent and OAm to prepare a reducing solution. The precursor solution and the reducing solution were then mixed and stirred until the reduction was complete, normally at 15–25 °C for 1 h. The as-made Au nanoparticles were precipitated by adding ethanol, collected by centrifugation, and washed with ethanol before characterizations.

As shown in Figs. 1 and S1 (Supporting information), high-quality monodisperse OAm-capped Au nanoparticles were obtained when *n*-hexane, or *n*-octane was used as the reaction solvent. Under the same synthetic conditions, monodisperse Au nanoparticles with average sizes of $(5.3 \pm 0.5)$ nm and $(5.6 \pm 0.4)$ nm were obtained in *n*-hexane and *n*-octane respectively. The obtained Au nanoparticles were even self-assembled into hexagonal monolayers on TEM grids. However, when tetralin, chloroform, or cyclohexane was used as the solvent, Au nanoparticles with much broader size dispersity were yielded (Fig. 1, Figs. S1–3 in Supporting information). In the case of tetralin, the formation of non-spherical Au nanoparticles were revealed in the products. A size
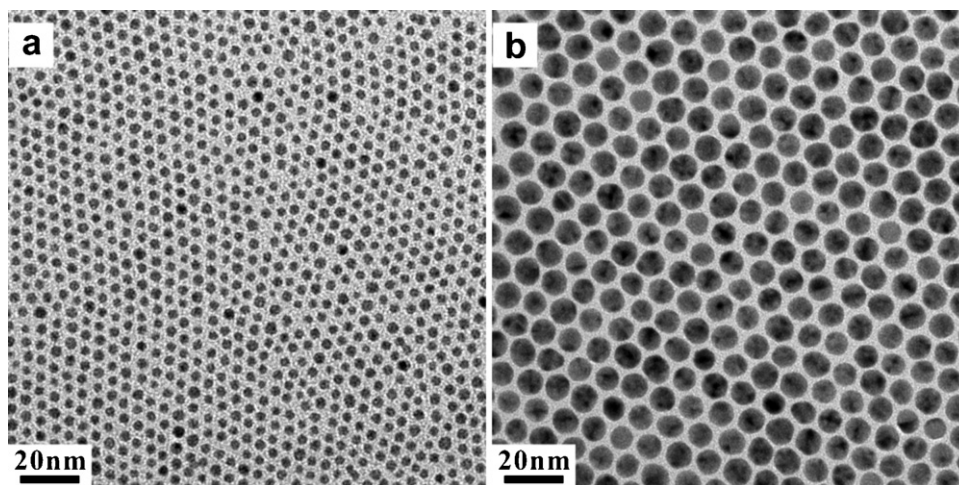
**Fig. 2.** TEM images of monodisperse OAm-capped Au nanoparticles obtained in *n*-octane under the same conditions except that different amounts of reductant TBAB were used: (a) 0.5 mmol, (b) 0.167 mmol.

increase from $(3.1 \pm 0.8)$ nm to $(5.8 \pm 1.8)$ nm was observed when the reaction temperature was lowered from 25 °C to 15 °C. Tuning the reaction temperature did not help much in optimizing the size dispersity of Au nanoparticles (Fig. S2 in Supporting information). Such a situation is quite different from previous report [18], suggesting that the synthesis of OAm-capped Au nanoparticles in tetralin is highly sensitive to the synthetic conditions. In linear hydrocarbons, however, a little change in synthetic condition did not significantly influence the quality of obtained Au nanoparticles. For example, in *n*-octane, increasing the temperature from 15 °C to 20 °C barely changed the size (from $(5.6 \pm 0.4)$ nm to $(5.5 \pm 0.4)$ nm) of Au nanoparticles (Fig. S4 in Supporting information). This is distinct from Sun's method in which tetralin was used as the solvent [18]. In Sun's method, the size of Au nanoparticles was highly dependent on the reaction temperature. A much larger size change (~1 nm) was resulted from a temperature change of 5 °C.

Although the synthesis of OAm-capped Au nanoparticles in linear hydrocarbons makes their size less sensitive to the reaction temperature than in tetralin, the average size of Au nanoparticles is easily tuned by the amount of the reducing agent while keeping all the other conditions the same. As shown in Fig. 2, reducing 0.25 mmol HAuCl$_4$ by various amount of TBAB in 11 mL OAm and 11 mL octane at 15 °C gave Au nanoparticles with different sizes. While doubling the amount of TBAB from 0.25 mmol to 0.50 mmol decreased the size of Au nanoparticles from $(5.6 \pm 0.4)$ nm to $(3.4 \pm 0.4)$ nm, reducing the amount of TBAB to 0.167 mmol

increased the particle size to $(8.1 \pm 0.6)$ nm (Fig. S5 in Supporting information). Although the size of Au nanoparticles was highly sensitive to the amount of TBAB used, the changed amount of TBAB did not alter the monodispersity of Au nanoparticles. Moreover, when the amount of TBAB was increased to 0.50 mmol, monodisperse Au nanoparticles with a similar size (3.3–3.6 nm) were obtained in *n*-hexane, *n*-octane and 1-octadecene at 15–25 °C (Fig. S6 in Supporting information).

As soon as a linear hydrocarbon is used as the solvent, OAm-capped Au nanoparticles with a narrow size distribution can be easily prepared even if there are some small changes in synthetic conditions. The remarkable solvent effect reported here has motivated us to figure out how the solvents influence the formation of OAm-capped Au nanoparticles. It should be noted that the importance of solvent in controlling the monodispersity of Au nanoparticle was not observed in the previously reported Au-thiol system [17]. The difference between thiol and amine-capping system might be caused by the different binding strength of thiol and amine on Au. The stronger binding of thiols on Au helps to create a compact protecting ligand layer on the surface of Au nanoparticles. In comparison, the binding of amine on Au is weaker, making the surface OAm protecting layer labile and subject to the influence of solvents. Based on the interaction with the OAm-capping layer on Au nanoparticles, hydrophobic solvents can be roughly classified into three different categories (Scheme 1): (1) linear hydrocarbons that can accumulate van der
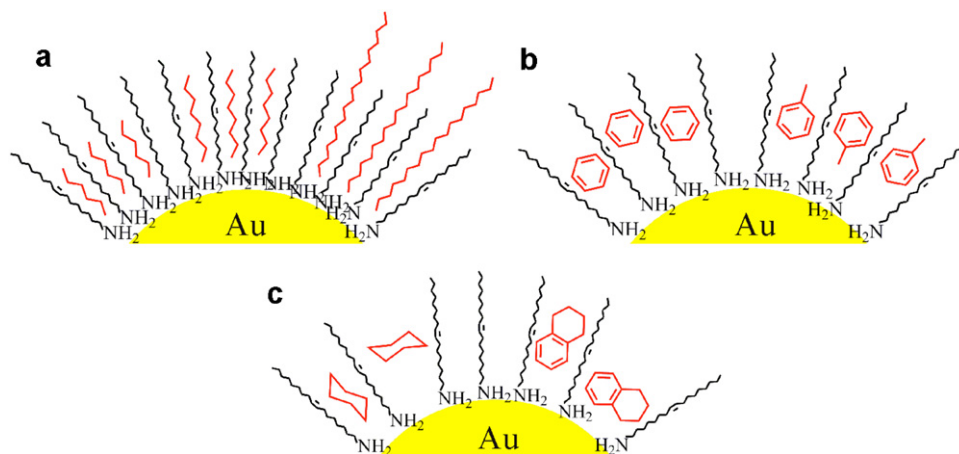


**Scheme 1.** Illustration of solvent effect on the Au-OAm interface in solvents with different molecular geometries (in red).
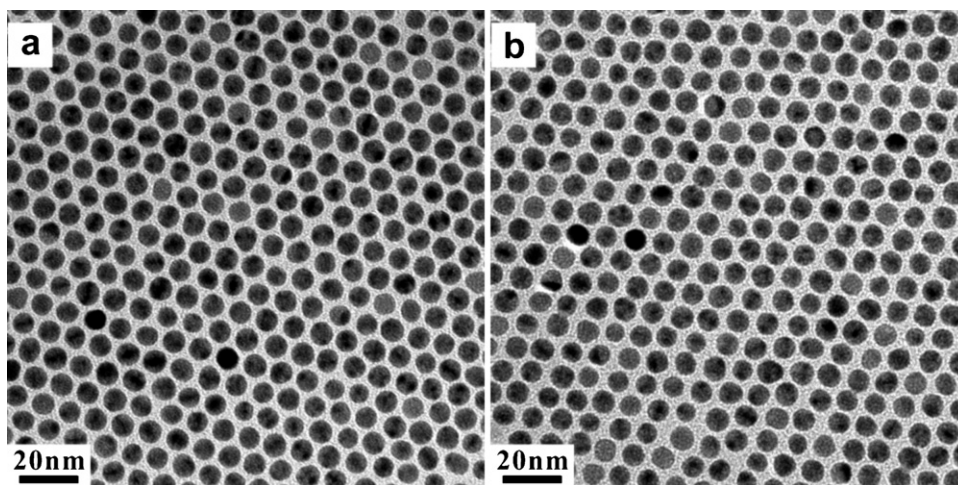
**Fig. 3.** TEM images of Au nanoparticles obtained in equal volume of OAm and (a) benzene, (b) toluene. The average size is (7.3 ± 0.4) nm and (7.2 ± 0.4) nm, respectively. Reaction conditions: 0.25 mmol HAuCl$_4$·4H$_2$O, 11 mL OAm, 11 mL selective solvent, 0.25 mmol TBAB, N$_2$ flow, 15 °C, 1 h.

Waals interactions with OAm chains to form a close-packed hydrophobic protection layer on Au surface; (2) simple aromatics, such as benzene and toluene, that are slightly bulky but still can be fixed in the OAm array; (3) other solvents (*e.g.*, tetralin, cyclohexane, chloroform) that can flip around to disturb the OAm layer. The solvent effect on the synthesis of OAm-capped Au nanoparticles described above could be caused by the different interactions between solvents and the surface OAm array on Au nanoparticles. It is worth noting that the unique interaction between the OAm array on metal nanoparticles and guest

molecules has been recently applied to control the selectivity of hydrogenation of $\alpha,\beta$-unsaturated aldehyde [24].

In order to evaluate the proposed mechanism, we have designed the following two series of experiments: (1) the reaction solvents were changed from linear hydrocarbons to planar aromatics; (2) monodisperse OAm-capped Au nanoparticles were pre-synthesized and used as the seeds for the preparation of larger Au nanoparticles in different types of solvents. In the first series of designed experiments, the solvent effect was demonstrated between linear hydrocarbons and aromatics. Similar to linear
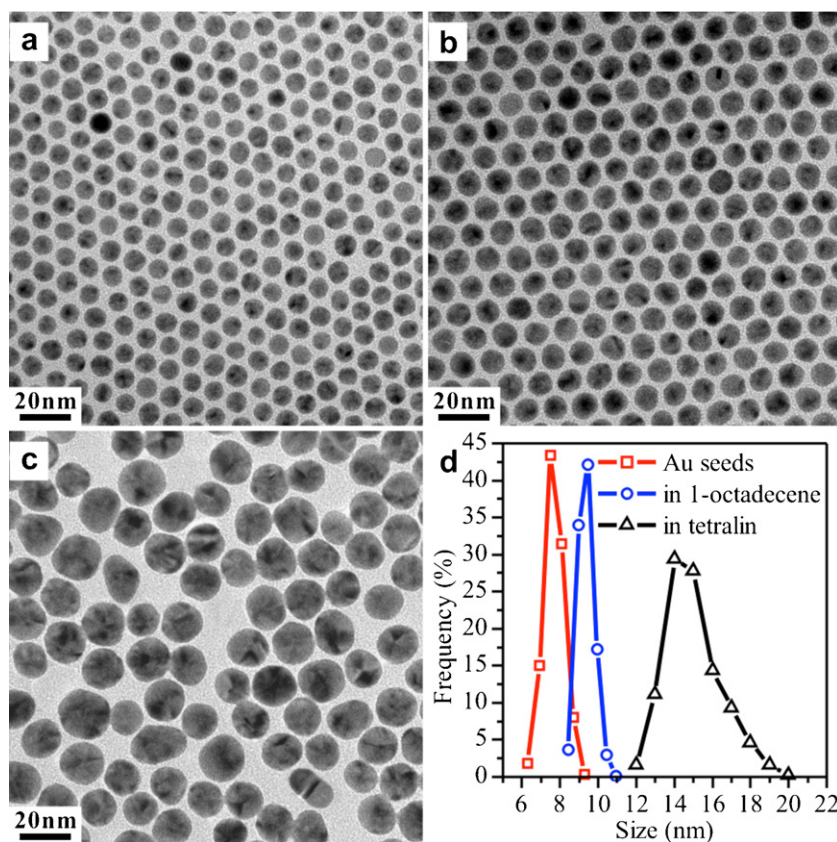


**Fig. 4.** Seeded growth of (a) 7.7 nm Au nanoparticles in different solvents: (b) 1-octadecene, or (c) tetralin. The average size is (7.7 ± 0.5) nm, (9.4 ± 0.4) nm and (15.0 ± 1.4) nm, respectively. (d) Comparison of size dispersity of samples shown in (a–c). Reaction conditions in seeded growth: 5 mL selective solvent, 0.5 mL OAm, 0.0625 mmol HAuCl$_4$·4H$_2$O, 1 mg 7.7 nm Au seeds, N$_2$ flow, 60 °C, 5 h.
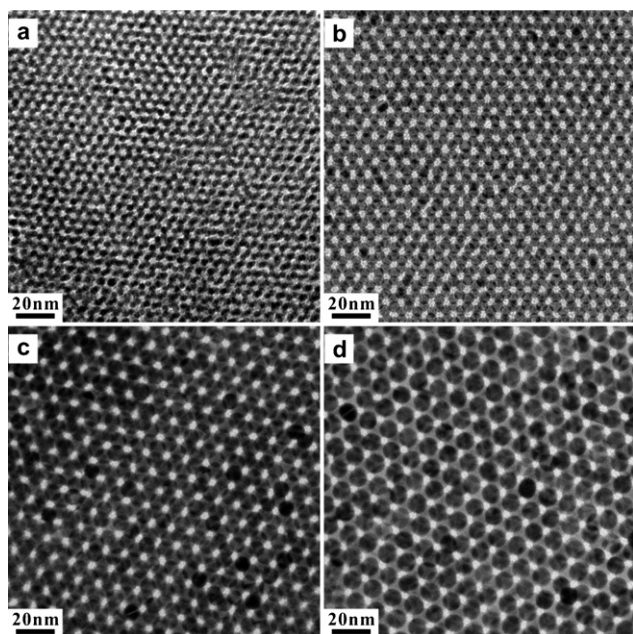
**Fig. 5.** Self-assembly of monodisperse Au nanoparticles with different sizes: (a) 3.4 nm, (b) 5.6 nm, (c) 8.1 nm, (d) 9.4 nm.

hydrocarbons, aromatics can have good interactions with carbon chain of OAm on the surface of Au nanoparticles, which should help to obtain monodisperse OAm-capped Au nanoparticles. Indeed, when the one-step growth was performed in benzene or toluene, high-quality monodisperse Au nanoparticles were also obtained (Fig. 3, Fig. S7 in Supporting information). However, the interaction of aromatic solvents (*e.g.*, benzene, toluene) would likely reduce the coverage of OAm on the surface of Au nanoparticles. The reduced OAm coverage could lead to fast deposition of Au atoms and thus formation of larger Au nanoparticles. As expected, Au nanoparticles obtained from the one-step synthesis in benzene and toluene had sizes of (7.3 ± 0.4) nm and (7.2 ± 0.4) nm, respectively. For comparison, under the same conditions, the average sizes of Au nanoparticles prepared in *n*-hexane and *n*-octane were (5.3 ± 0.5) nm and (5.6 ± 0.4) nm, respectively. While good interaction between OAm and solvent molecules is important to the preparation of monodisperse OAm-capped Au nanoparticles, the size of solvents can determine the size of obtained Au nanoparticles. These results confirm our proposed mechanism for the observed solvent effect.

In the second series of experiments, the seeded growth of larger Au nanoparticles from monodisperse 7.7 nm Au nanoparticles were carried out at 60 °C in 1-octadecene and tetralin for comparison. In the seeded growth process, OAm served as both capping agent and reducing agent. As shown in Fig. 4, in 1-octadecene, monodisperse Au nanoparticles with an average size of (9.4 ± 0.4) nm were obtained in 5 h, which can be explained by the presence of compact hydrophobic protecting layer formed by OAm and 1-octadecene. In tetralin, however, the similar growth condition led to the formation of much larger Au nanoparticles with a much wider dispersity (12–20 nm) (Fig. 4c). Similar to the one-step growth of Au nanoparticles in tetralin, the formation of some non-spherical Au nanoparticles was observed. These results suggest that in tetralin the seeded growth occurred rather rapidly but inhomogeneously on the surface of Au nanoparticulate seeds, which might be explained by the lack of a close-packed protecting layer due to interruption from tetralin molecules (Scheme 1).

Once a right solvent is used, the size of obtained Au nanoparticles is less sensitive to small change in reaction temperature. More importantly, while keeping decent monodispersity, the size of Au nanoparticles can be easily controlled by the amount of reducing agent and also seeded growth. The obtained different-sized monodisperse Au nanoparticles are readily assembled into ordered superlattices (Fig. 5). Such a feature makes the developed method highly desirable for the preparation of monodisperse amine-capped Au nanoparticles for various applications, particularly for size-dependent studies.

## 4. Conclusion

In conclusion, we have revealed a remarkable solvent effect in the one-phase synthesis of OAm-capped Au nanoparticles using amine-borane complex as the reducing agent. The selective use of linear hydrocarbons or planar aromatics as the reaction solvent is critical to obtaining monodisperse Au nanoparticles. The revealed solvent effect allows facile production of high-quality amine-capped Au nanoparticles in a more controllable and repeatable manner.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2013.03.054.

## References

[1] M.C. Daniel, D. Astruc, Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology, Chem. Rev. 104 (2003) 293–346.

[2] M.R. Jones, K.D. Osberg, R.J. Macfarlane, M.R. Langille, C.A. Mirkin, Templated techniques for the synthesis and assembly of plasmonic nanostructures, Chem. Rev. 111 (2011) 3736–3827.

[3] C.J. Jia, F. Schuth, Colloidal metal nanoparticles as a component of designed catalyst, Phys. Chem. Chem. Phys. 13 (2011) 2457–2487.

[4] M. Comotti, W.C. Li, B. Spliethoff, F. Schuth, Support effect in high activity gold catalysts for CO oxidation, J. Am. Chem. Soc. 128 (2006) 917–924.

[5] J.F. Liu, W. Chen, X.W. Liu, K.B. Zhou, Y.D. Li, Au/LaVO₄ nanocomposite: preparation, characterization, and catalytic activity for CO oxidation, Nano Res. 1 (2008) 46–55.

[6] B.H. Wu, H. Zhang, C. Chen, S.C. Lin, N.F. Zheng, Interfacial activation of catalytically inert Au (6.7 nm)–Fe₃O₄ dumbbell nanoparticles for CO oxidation, Nano Res. 2 (2009) 975–983.

[7] Y.M. Liu, H. Tsunoyama, T. Akita, S.H. Xie, T. Tsukuda, Aerobic oxidation of cyclohexane catalyzed by size-controlled Au clusters on hydroxyapatite: size effect in the sub-2 nm regime, ACS Catal. 1 (2010) 2–6.

[8] H.Y. Fan, K. Yang, D.M. Boye, et al., Self-assembly of ordered, robust, three-dimensional gold nanocrystal/silica arrays, Science 304 (2004) 567–571.

[9] E.V. Shevchenko, D.V. Talapin, N.A. Kotov, S. O'Brien, C.B. Murray, Structural diversity in binary nanoparticle superlattices, Nature 439 (2006) 55–59.

[10] A.M. Kalsin, M. Fialkowski, M. Paszewski, S.K. Smoukov, K.J.M. Bishop, B.A. Grzybowski, Electrostatic self-assembly of binary nanoparticle crystals with a diamond-like lattice, Science 312 (2006) 420–424.

[11] R.J. Macfarlane, B. Lee, M.R. Jones, et al., Nanoparticle superlattice engineering with DNA, Science 334 (2011) 204–208.

[12] X.C. Ye, J. Chen, C.B. Murray, Polymorphism in self-assembled AB6 binary nanocrystal superlattices, J. Am. Chem. Soc. 133 (2011) 2613–2620.

[13] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, Synthesis of thiol-derivatised gold nanoparticles in a two-phase liquid–liquid system, J. Chem. Soc., Chem. Commun. (1994) 801–802.

[14] S. Stoeva, K.J. Klabunde, C.M. Sorensen, I. Dragieva, Gram-scale synthesis of monodisperse gold colloids by the solvated metal atom dispersion method and digestive ripening and their organization into two- and three-dimensional structures, J. Am. Chem. Soc. 124 (2002) 2305–2311.

[15] X.G. Peng, N.R. Jana, Single-phase and gram-scale routes toward nearly monodisperse Au and other noble metal nanocrystals, J. Am. Chem. Soc. 125 (2003) 14280–14281.

[16] I. Hussain, S. Graham, Z.X. Wang, et al., Size-controlled synthesis of near-monodisperse gold nanoparticles in the 1–4 nm range using polymeric stabilizers, J. Am. Chem. Soc. 127 (2005) 16398–16399.

[17] N.F. Zheng, J. Fan, G.D. Stucky, One-step one-phase synthesis of monodisperse noble-metallic nanoparticles and their colloidal crystals, J. Am. Chem. Soc. 128 (2006) 6550–6551.

[18] S. Peng, Y.M. Lee, C. Wang, et al., A facile synthesis of monodisperse Au nano-particles and their catalysis of CO oxidation, Nano Res. 1 (2008) 229–234.

[19] C.M. Shen, C. Hui, T.Z. Yang, et al., Monodisperse noble-metal nanoparticles and their surface enhanced raman scattering properties, Chem. Mater. 20 (2008) 6939–6944.

[20] X. Huang, X. Zhou, S. Wu, et al., Reduced graphene oxide-templated photochemi-cal synthesis and in situ assembly of Au nanodots to orderly patterned Au nanodot chains, Small 6 (2010) 513–516.

[21] A. Sugie, T. Somete, K. Kanie, A. Muramatsu, A. Mori, Triethylsilane as a mild and efficient reducing agent for the preparation of alkanethiol-capped gold nanopar-ticles, Chem. Commun. (2008) 3882–3884.

[22] X.M. Hou, X.L. Zhang, S.T. Chen, et al., Size-controlled synthesis of Au nanopar-ticles and nanowires and their application as SERS substrates, Colloids Surf. A 384 (2011) 345–351.

[23] J. Song, D. Kim, D. Lee, Size control in the synthesis of 1–6 nm gold nanoparticles via solvent-controlled nucleation, Langmuir 27 (2011) 13854–13860.

[24] B.H. Wu, H.Q. Huang, J. Yang, N.F. Zheng, G. Fu, Selective hydrogenation of $\alpha,\beta$-unsaturated aldehydes catalyzed by amine-capped platinum–cobalt nanocrys-tals, Angew. Chem. Int. Ed. 51 (2012) 3440–3443.