Synthesis of gold nanoparticles within a supramolecular gel-phase network†

Christine S. Love,[a] Victor Chechik,*[a] David K. Smith,*[a] Karen Wilson,[a] Ian Ashworth[b] and Colin Brennan[b]

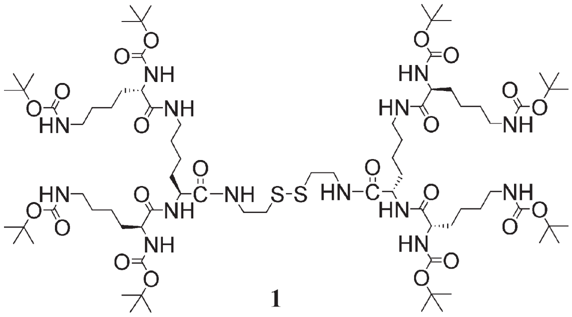
Received (in Cambridge, UK) 3rd December 2004, Accepted 10th February 2005
First published as an Advance Article on the web 22nd February 2005
DOI: 10.1039/b418190e

Gold nanoparticles with diameters of *ca.* 13 nm were synthesised by UV irradiation of a supramolecular organogel into which $HAuCl_4$ and tetraoctylammonium bromide had been diffused—the gel network plays an essential role in nanoparticle stabilisation.

Controlling the synthesis of nanoscale objects is one of the most important challenges facing modern chemistry.[1] In several prominent examples, supramolecular organogels, which consist of multiple self-assembled entangled fibres, have been employed to influence the shape and nanostructure of inorganic materials.[2] In many cases, the inorganic nanostructures which are formed resemble the fibrous gel network. For example, the groups of Shinkai,[3] Hanabusa[4] and Stupp[5] have developed helical silica fibres, transition metal oxide nanotubes and helical CdS ribbons, respectively. Metals have also been templated on gel-phase materials in this way, with Liu and co-workers reporting silver nanowires.[6] However, not all of the inorganic structures generated in this way are simple fibres—Lu and co-workers reported the formation of 'pearl-necklace' architectures of CdS, with inorganic nanoparticles having diameters of approximately 30 nm being apparently linked by a fibre of the organogel.[7]

It was with some surprise that we noted there was only one report of the use of supramolecular gels for the construction of gold nanostructures.[8] Kimura, Shirai and co-workers heated a gelator with peripheral thiol groups with a sample of small (1.7 nm) octanethiol stabilised nanoparticles, and on cooling a brown gel resulted. TEM analysis indicated that the small gold nanoparticles had been bound to the fibrous gel-phase network as a consequence of ligand exchange. There has been extensive development of methods for the synthesis of gold nanoparticles in recent years,[9] however the vast majority of these methods give rise to relatively small nanoparticles (*ca.* 1–10 nm). With interest in controlling nanoparticle synthesis and assembly, we therefore decided to investigate the ability of our recently reported gelator **1** (Fig. 1)[10] to control the synthesis and modify the architectures of nanoscale assemblies constructed from gold. Initially, we thought that both the disulfide and the presence of the gel may have impacts on the gold structures.

As reported previously, compound **1** forms gel-phase materials in toluene.[10] In order to 'load' these organogels with an effective precursor for the synthesis of gold nanostructures, a diffusion method was used. $HAuCl_4$ was transferred into toluene using tetraoctylammonium bromide (TOAB) and then the solution was allowed to stand above a sample of gel. The yellow coloration was observed to diffuse slowly (days) into the gel until an even distribution (as monitored by visual observation of the sample) was obtained. The excess toluene was then removed from the top of the gel. The thermal properties of the gel remained the same after the diffusion process, indicating that Au(III) and the phase transfer agent do not significantly affect the macroscopic gel-phase materials properties. The gel was then irradiated with a 100 W mercury vapour UV lamp. UV irradiation is known to reduce metal salts to form nanoparticles in the presence of a suitable stabiliser.[11]



1

Fig. 1 Dendritic gelator **1**.

On irradiation, there were two visually observable changes to the gel. Firstly, the colour rapidly changed from orange–yellow to colourless (*ca.* 30 min). The second change was more dramatic, with the gel changing from colourless to intense purple (Fig. 2) over a period of about six hours. These processes could also be monitored using UV-visible spectrometry (Fig. 2). It is proposed that these changes are consistent with an initial rapid reduction of Au(III) to Au(I), followed by slow reduction from Au(I) to Au(0). Furthermore, the presence of an absorption band at 550 nm is suggestive of the presence of relatively large nanosized gold aggregates within the gel-phase network. The final sample appeared as a coloured purple band running through the gel—possibly a result of the reaction occurring where the UV radiation was most intense. Notably the band did not diffuse, even over extended periods of time (weeks). It is worth noting that small organic molecules (such as azobenzene) diffuse very rapidly in and out of the gel-phase material. This would indicate that the nanoscale Au(0) generated on irradiation is unable to diffuse through the fibrous gel-phase network. This could either be a consequence of it having a large size relative to the inter-fibre

---

† Electronic supplementary information (ESI) available: Histogram of gold nanoparticle diameters and XPS spectra including deconvolution of the Au peaks for the gold colloid product in the gel. See http://www.rsc.org/suppdata/cc/b4/b418190e/
*vc4@york.ac.uk (Victor Chechik)
dks3@york.ac.uk (David K. Smith)

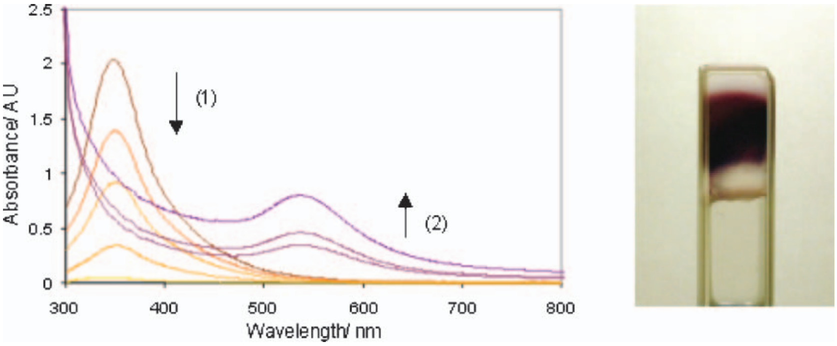


Fig. 2 UV-visible spectra on irradiation of $HAuCl_4$ and TOAB in toluene gelated by compound **1**. The spectra illustrate (1) the loss of colour as Au(III) is reduced to Au(I) and (2) the increase in the surface plasmon band as Au(0) nanoparticles are formed. The photo illustrates the purple band formed on irradiation.

spacing, or alternatively having significant interactions with the gel fibres.

X-Ray photoelectron spectroscopy (XPS) performed on the gel samples at different stages of the experiment was used to confirm our assignment of the redox processes occurring on irradiation (the spectra can be found in the supplementary information†). The initial Au(III) was converted to the intermediate colourless material which was composed of a single Au species with a binding energy consistent with Au(I) (Table 1).[12] Following further UV irradiation the XPS band progressively shifted to lower binding energy. The Au 4f spectra for the final nanoparticles could be deconvoluted into states consistent with Au(0) colloids and a residual amount of unreduced Au(I). The binding energy of the Au(0) colloids is observed ≈0.5 eV below that for bulk Au, consistent with that expected for the Au surface state.[13] The gel stabilised nanoparticles also exhibit a small contribution due to bulk Au (0) which is attributed to the signal from the Au core.

In order to shed further light on the nature of the Au(0) species formed, transmission electron microscopy (TEM) was performed. Using this technique, gold nanoparticles were visualised (Fig. 3). These particles had fairly uniform size, with an average diameter of 13 nm (measured over *ca.* 100 nanoparticles). This relatively large diameter is supported by the purple colouration and relatively intense surface plasmon band at 550 nm—consistent with relatively large nanoscopic gold assemblies. There was no noteworthy ordering of the nanoparticles (although a few clusters were observed). This may indicate that the particles form in pockets of solvent within the gel structure rather than on the surface of the fibres themselves.

Interestingly, if a sample of $HAuCl_4$ and TOAB in toluene was irradiated under the same conditions, only in the absence of a gelator, a loss of colour was initially observed, and over a period of several days, a gold sheen appeared on the walls of the cuvette. This indicates that reduction to Au(0) still occurs, but that macroscopic bulk gold is formed, rather than well-defined nanoparticles, with nucleation taking place on the walls of the cuvette. This illustrates that the gel network appears to play a role in preventing nanoparticle aggregation.

Table 1 Binding energies and assignments of Au species within the supramolecular gel-phase network. Final composition based on spectral deconvolution is shown in brackets

	Au $4f_{7/2}$ binding energy/eV		
Assignment	Starting material	Intermediate gel	Final gel (% composition Au)
Au(III)	84.8		
Au(I)		84.4	84.4 (37.9%)
Bulk Au			84.0 (8.6%)
Au colloid			83.5 (53.5%)

We then investigated the purple gel containing the nanoparticles in more detail. On heating the gel above its T_{gel} value, it was converted into a sol. At this point, the purple nanoparticles collapsed to form an insoluble black precipitate. Equally, if methanol was added to the gel, causing its structure to break down, a black precipitate was once again observed. These observations indicate that it is the gel network which plays an active role in stabilising the gold nanoparticles, and that once this network is removed, the nanoparticles are no longer stable with respect to aggregation. Interestingly, however, if octanethiol was diffused into the gel before the addition of methanol, a purple suspension was formed rather than a black precipitate. This indicates that a degree of stabilisation of the 13 nm gold nanoparticles inside the gel could be achieved by the thiol-stabiliser before the gel was broken down.

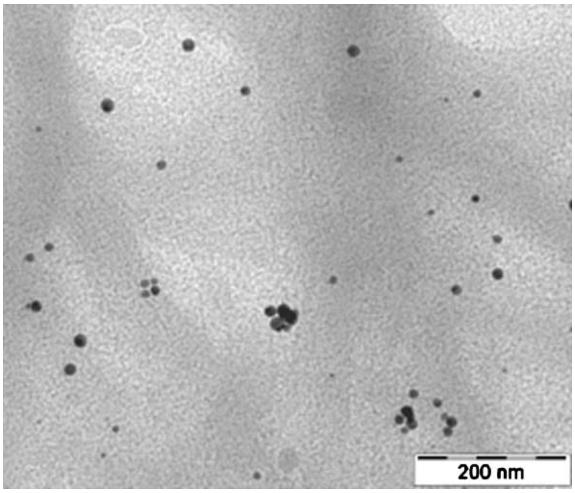
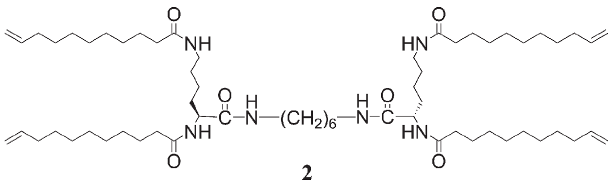


Fig. 3 TEM image of nanoparticles formed within the gel. Sample was prepared by drying the purple gel-phase network containing the nanoparticles. A histogram showing the nanoparticle size distribution is available in the supplementary information.†



2

Fig. 4 Dendritic gelator **2**.

We were interested to know whether the molecular structure of the gelator was playing a role in controlling the formation of gold nanoparticles. In particular, we thought the disulfide bridge might be interacting specifically with Au(0)—indeed, we have already reported that such dendritic ligands can act as nanoparticle stabilisers in solution.[14] We therefore attempted nanoparticle synthesis in a gel formed using compound **2**,[15] which also acts as an effective organogelator in toluene, yet has no sulfur atoms within its structure (Fig. 4). Once again, a purple colouration was observed, and the results were directly analogous to those obtained using gelator **1**—indicating that large Au(0) particles were still being formed. We can therefore conclude that the nanoparticle stabilisation is being achieved by the fibrous gelator network itself, rather than specific interactions with the individual molecular building blocks which constitute the supramolecular gel.

In summary, this paper offers a synthetic approach to gold nanoparticles of *ca.* 13 nm. These nanoparticles appear to be stabilised by, and immobilised within, a supramolecular gel-phase network. As well as offering an intriguing approach to the synthesis of gold nanostructures, this paper also shows how hybrid organic–inorganic materials consisting of both organic fibres and inorganic nanoparticles can readily be generated using this simple irradiative methodology. We postulate that this approach may, in the future, generate materials with interesting optoelectronic applications, such as immobilised addressable nanoparticles, or gels with applications in sensor technology. Furthermore, modification of the peripheral groups on the gelator fibres may allow specific interactions between the organic and inorganic parts of these new hybrid materials, in order to yield systems with an additional degree of nanostructuring.

Christine S. Love,[a] Victor Chechik,*[a] David K. Smith,*[a] Karen Wilson,[a] Ian Ashworth[b] and Colin Brennan[b]
[a]*Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: vc4@york.ac.uk; dks3@york.ac.uk*
[b]*Syngenta, Technology and Projects, Huddersfield, UK HD2 1FF*

Notes and references

1 See for example: (*a*) A. H. Flood, R. J. A. Ramirez, W. Q. Deng, R. P. Muller, W. A. Goddard and J. F. Stoddart, *Aust. J. Chem.*, 2004, **57**, 301–322; (*b*) I. W. Hamley, *Angew. Chem., Int. Ed.*, 2003, **42**, 1692–1712; (*c*) J. A. A. W. Elemans, A. E. Rowan and R. J. M. Nolte, *J. Mater. Chem.*, 2003, **13**, 2661–2670; (*d*) S. A. Davis, M. Breulmann, K. H. Rhodes, B. Zhang and S. Mann, *Chem. Mater.*, 2001, **13**, 3218–3226.

2 K. J. C. van Bommel, A. Friggeri and S. Shinkai, *Angew. Chem., Int. Ed.*, 2003, **42**, 980–999.

3 (*a*) Y. Ono, K. Nakashima, M. Sano, Y. Kanekiyo, K. Inoue, J. Hojo and S. Shinkai, *Chem. Commun.*, 1998, 1477–1478; (*b*) J. H. Jung, Y. Ono and S. Shinkai, *Angew. Chem., Int. Ed.*, 2000, **39**, 1862–1865; (*c*) K. Sugiyasu, S. Tamura, M. Takeuchi, D. Berthier, I. Huc, R. Oda and S. Shinkai, *Chem. Commun.*, 2002, 1212–1213.

4 (*a*) S. Kobayashi, K. Hanabusa, N. Hamasaki, M. Kimura, H. Shirai and S. Shinkai, *Chem. Mater.*, 2000, **12**, 1523–1525; (*b*) S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shirai and K. Hanabusa, *J. Am. Chem. Soc.*, 2002, **124**, 6550–6551.

5 E. D. Sone, E. R. Zubarev and S. I. Stupp, *Angew. Chem., Int. Ed.*, 2002, **41**, 1705–1709.

6 C. L. Chan, J. B. Wang, J. Yuan, H. Gong, Y. H. Liu and M. H. Liu, *Langmuir*, 2003, **19**, 9440–9445.

7 P. C. Xue, R. Lu, Y. Huang, M. Jin, C. H. Tan, C. Y. Bao, Z. M. Wang and Y. Y. Zhao, *Langmuir*, 2004, **20**, 6470–6475.

8 M. Kimura, S. Kobayashi, T. Kuroda, K. Hanabusa and H. Shirai, *Adv. Mater.*, 2004, **16**, 335–338.

9 (*a*) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *Chem. Commun.*, 1994, 801–802; (*b*) Z. Y. Zhong, K. B. Male and J. H. T. Luong, *Anal. Lett.*, 2003, **36**, 3097–3118.

10 C. S. Love, A. R. Hirst, V. Chechik, D. K. Smith, I. Ashworth and C. Brennan, *Langmuir*, 2004, **20**, 6580–6585.

11 (*a*) K. Torigoe and K. Esumi, *Langmuir*, 1992, **8**, 59–63; (*b*) K. Esumi, A. Suzuki, N. Aihara, K. Usui and K. Torigoe, *Langmuir*, 1998, **14**, 3157–3159.

12 M.-C. Bourg, A. Badia and R. B. Lennox, *J. Phys. Chem. B*, 2000, **104**, 6562–6567.

13 P. H. Citrin, G. K. Wertheim and Y. Baer, *Phys. Rev. B*, 1983, **27**, 3160–3175.

14 C. S. Love, V. Chechik, D. K. Smith and C. Brennan, *J. Mater. Chem.*, 2004, **14**, 919–923.

15 Full details of the synthesis and gelation behaviour of compound **2** will be reported in due course.