Au nanoparticle-imprinted polymers

Stéphanie Koenig and Victor Chechik*

Received (in Cambridge, UK) 4th March 2005, Accepted 20th June 2005
First published as an Advance Article on the web 14th July 2005
DOI: 10.1039/b503243a

Au nanoparticles protected with a polymerisable ligand were incorporated into bulk macroporous polymers; etching the metal core resulted in disulfide-lined, nanometre-scale cavities capable of recognising similarly-sized Au particles.

Thiol-protected Au nanoparticles are extremely versatile supramolecular structures. The strength of the Au–S bond and the relatively low reactivity of the Au surface make it possible to incorporate virtually any functional group in the ligand structure.[1] The synthetic procedure is also very simple; Au nanoparticles 2–5 nm in diameter with a very well-defined structure can be prepared and purified in just a few hours.[2] Arguably, Au nanoparticles are the easiest to make yet versatile large supramolecular assemblies. Therefore, in the last decade such materials became a very popular subject for study.

Most research effort is directed towards exploiting the functionalities at the nanoparticle surface, or the properties of the metal core. The core material, however, can also be used as a sacrificial template. For instance, the organic ligands assembled around the Au core template, can be cross-linked by polymerisation or reaction with polyfunctional reagents.[3] Following the cross-linking, the sacrificial template can be removed by etching. Au is a convenient sacrificial template, as it can be etched readily by a mild oxidising reagent (*e.g.*, $[Fe(CN)_6]^{3-}$, I_2, O_2) in the presence of a good ligand (*e.g.*, CN^-, I^-, $S_2O_3^{2-}$).[4] This procedure leads to hollow organic nanometre-scale capsules.

A number of strategies for the preparation of such nanocapsules have been reported by us and others.[5] This research, however, was hampered by two general problems: difficult characterisation and poor solubility. The structure of nanometre-scale capsules can only be proved using microscopy, but they are difficult to visualise using electron microscopy due to poor contrast. Therefore, AFM has been instrumental in characterising these materials.

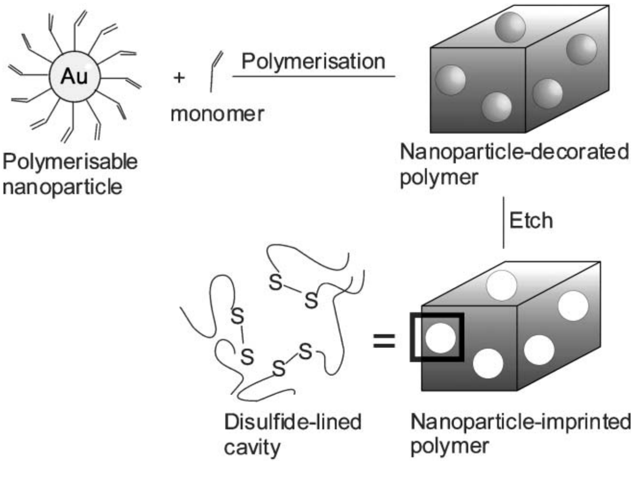
We found that etching the metal core from shell cross-linked Au nanoparticles often results in insoluble materials. To overcome this problem, we decided to incorporate the shell cross-linked nanoparticles into bulk polymers. Etching of the Au core from these materials effectively results in nanoparticle-imprinted polymers.

Incorporation of Au nanoparticles into polymers has been previously achieved using several strategies. Simple blending of nanoparticles with polymers often leads to aggregation, although Lennox *et al.* succeeded in dispersing polystyrene-coated particles in a polystyrene matrix.[6] Polymer-embedded particles could also be prepared by reduction of metal salts in a molten polymer;[7] however this strategy cannot produce the cross-linked shell required for the preparation of nanoparticle-imprinted polymers. Addition of Au nanoparticles to polymerisation mixtures also leads to their incorporation into polymers.[8]

We chose an alternative strategy for chemically linking nanoparticles with a polymer matrix, which includes polymerisation of a monomer around the nanoparticles coated with a polymerisable ligand. In this reaction, the organic shell will be cross-linked and incorporated into bulk polymer structure during polymerisation (Scheme 1). A similar approach has recently been used to prepare Au nanoparticle-imprinted silica.[9]

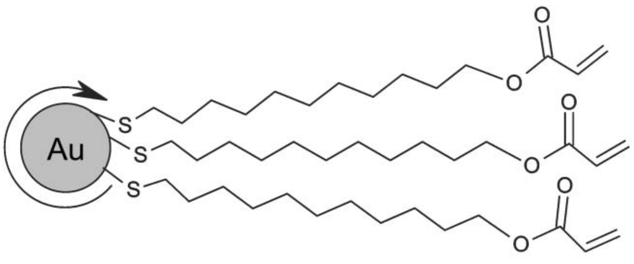
We used free radical polymerisation to polymerise a monomer around nanoparticles **1** modified with an acrylate-functionalised ligand (Fig. 1).[10] Radical polymerisation is usually quite inefficient on the surface of thiol-protected nanoparticles. For instance, we were unable to achieve efficient free radical polymerisation of adjacent acrylate ligands on the surface of nanoparticle **1** (*e.g.*, in the absence of additional monomers), despite some literature reports of successful polymerisation in Au-thiol self-assembled monolayers.[11] This is probably due to chain transfer to the thiolate ligands leading to nanoparticle aggregation. In the absence of additional monomers, the efficiency of polymerisation was further reduced by high concentration of initiator (as the concentration of nanoparticle is quite low, a relatively high concentration of initiator was required to achieve a reasonable polymerisation rate).

However, co-polymerisation of acrylate-terminated nanoparticles **1** with bulk monomers proceeded without aggregation. In the presence of free monomers, low concentration of initiator can be used. Besides, rapid increase in viscosity during this co-polymerisation further helped to prevent aggregation.



Scheme 1 Preparation of nanoparticle-imprinted polymers.

Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: vc4@york.ac.uk; Fax: +44 1904 432516; Tel: +44 1904 434185



1

Fig. 1 Au nanoparticle protected by an acrylate-functionalised ligand.

In order to allow etching of the polymer-embedded Au particles, the polymer must be solvent-permeable and hence highly porous. In conventional imprinted polymers the porosity is usually achieved by addition of a porogen to the polymerisation mixture.[12] Typical porogens are volatile organic solvents. After initial oligomerisation, the polymers phase-separate from the solution, so that the solvent phase leaves pores in the polymer structure. The solvent is then removed from the polymer by evaporation.

Imprinted polymers must have a very rigid structure to maintain the shape of the sacrificial template after its removal. Therefore, large quantities of cross-linking agent are used.[13]

We prepared a series of macroporous polymers decorated with Au nanoparticles **1**. The polymers were based on polystyrene or dimethylacrylamide cross-linked with ethylene glycol dimethacrylate (EGDMA). The polymerisation (initiated by AIBN) was carried out at 60 °C. Acetone was used as porogen. The cross-linker : monomer : porogen ratio was 1 : 0.35 : 1 to ensure efficient cross-linking and high porosity of the polymer. An example of the polymers is shown in Fig. 2a, it was bluish grey in colour. The polymers were characterised by scanning and transmission electron microscopy. The corresponding images are shown in Fig. 2b and 3.

The pores are clearly visible in the images; they vary in size between 50 and 200 nm (Fig. 3a). Zooming in on the TEM image shows the polymer-embedded Au nanoparticles (Fig. 3b). The number of nanoparticles in the field of view is too small to carry out a reliable analysis of size distribution (the nanoparticle density is consistent with the stoichiometry of the polymerisation mixture); however the average size is *ca.* 1.9 ± 0.6 nm, similar to the size of the original nanoparticles. Importantly, this confirms the absence of nanoparticle aggregation during free radical polymerisation (Fig. 3b).

To further characterise the nanoparticle-containing polymer, we recorded its powder UV-Vis spectrum (Fig. 4a) using a diffuse-reflectance technique. For comparison, Fig. 4b also shows a solution spectrum of a similar non-cross-linked polymer (*e.g.*, polystyrene prepared under identical conditions but in the absence of cross-linker and porogen). The substantially different spectral line shape of the powder sample (Fig. 4a) is probably due to strong wavelength-dependence of light scattering by the macroporous polymer (*e.g.*, with pore size comparable or smaller than the wavelength of light).[14] Nonetheless, both spectra show plasmon peak at *ca.* 520 nm (as a shoulder), which confirms the absence of nanoparticle aggregation in the polymer.

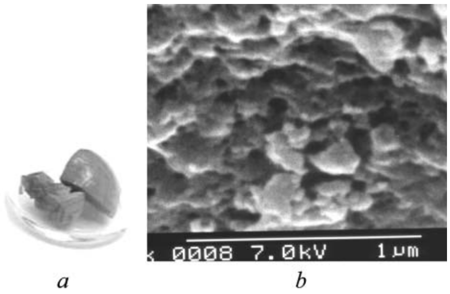


Fig. 2 A photograph (a) and SEM image (b) of Au nanoparticle-decorated macroporous EGDMA cross-linked polystyrene.

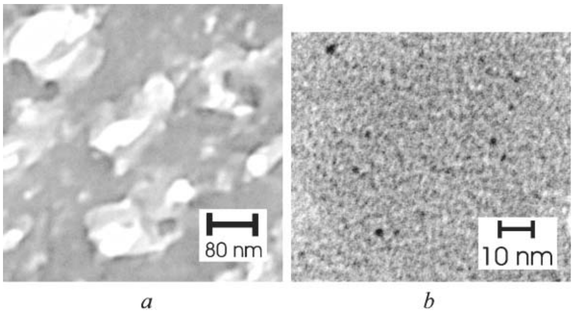


Fig. 3 TEM images of nanoparticle-decorated, macroporous EGDMA cross-linked polystyrene.

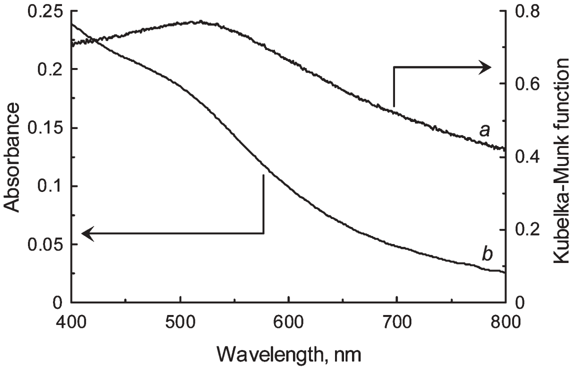


Fig. 4 Diffuse-reflectance UV-Vis spectrum of nanoparticle-containing cross-linked polystyrene (a), and solution UV-Vis spectrum of nanoparticle-containing non-cross-linked polystyrene (b).

In order to remove the sacrificial Au template from the polymers, they were cryogenically ground (to increase surface area) and treated with a solution of I_2 in aqueous KI. Iodine is known to be capable of oxidising Au nanoparticles to a mixture of Au(I) and Au(III) iodides, depending on the stoichiometry and reaction conditions.[15] After washing, the excess iodine was quenched by aqueous $Na_2S_2O_3$. We found that 30 min exposure to iodine etched most nanoparticles (as judged by the loss of bluish grey colour). Overnight treatment was sufficient to produce white, gold-free polymer powder.

Further evidence for the successful removal of gold from the polymer was obtained by ICP-OES analysis of the aqueous extract of the polymer samples digested with *aqua regia*. The amount of gold present in nanoparticle-containing polymers was *ca.* 400 ppm. After etching, the gold content was reduced to *ca.* 50 ppm. Incomplete removal of gold is probably due to rather strong adsorption of Au(III) by the polymer.

In order to visualise the etching process, we treated the microtomed sections of the polymer deposited on the TEM grid, with iodine/KI solution. The exposure time was reduced to 30 s to prevent damage to the TEM grid. Due to the small thickness of the microtomed sections, this exposure time was sufficient to etch the nanoparticles as shown in Fig. 5a.

We found that the etching process strongly depends on the hydrophilicity of the polymer. For instance, while Au nanoparticles incorporated into EGDMA cross-linked polystyrene or polydimethylacrylamide, reacted readily with iodine, we were unable to etch Au from polystyrene cross-linked with hydrophobic divinylbenzene.

The polymers after removal of the template should possess cavities *ca.* 2 nm in diameter. The high concentration of the cross-linker (EGDMA) in the polymerisation mixtures ensures very high rigidity; the cavities should hence retain their structure after removal of the template. Moreover, oxidative etching of nanoparticles with iodine is known to release the ligands as disulfides. In a control experiment, we showed that treatment of Au nanoparticles with iodine before polymerisation indeed resulted in formation of acrylate-terminated disulfide. The cavities in the nanoparticle-imprinted polymer should therefore be lined with disulfide bonds.

In order to test the host properties of the nanoparticle-imprinted polymer, we treated it with several types of Au nanoparticles: citrate-stabilised aqueous nanoparticles 13 nm in diameter;[16] a toluene solution of butanethiol-stabilised particles *ca.* 2.5 nm in diameter, and CH_2Cl_2-dissolved PPh_3-protected nanoparticles *ca.* 1.4 nm in diameter.[17] After 10 min exposure, the polymer powders were repeatedly washed with the corresponding solvents and dried. Control experiments were carried out for all mixtures using identical macroporous polymers prepared in the absence of Au nanoparticles.

We observed that all blank polymers and most nanoparticle-imprinted polymers remained colourless after treatment. However, nanoparticle-imprinted, EGDMA cross-linked polydimethylacrylate become grey after staining with PPh_3-protected particles, indicating that some nanoparticles are adsorbed in the pores. In order to characterise the polymer, it was embedded into an acrylic resin, microtomed and imaged by TEM (Fig. 5b). ICP-OES analysis of this polymer revealed the presence of $>$2000 ppm of Au. The rather large amount of gold is probably due to partial aggregation of Au nanoparticles in the polymer.

The failure of blank polymers to adsorb Au nanoparticles is not surprising. Although the pores in the polymer structure are large enough to accommodate the nanoparticles, the polymer has no functional groups which could strongly adhere to Au nanoparticles. The nanoparticle-imprinted polymers have cavities with many disulfide bonds on the surface, which have strong affinity for Au. However, the size of the cavities is much smaller than that of citrate-protected Au nanoparticles, which explains the failure of the polymer to adsorb these particles. Butanethiol-stabilised particles should fit in the cavities; however disulfides are known to be virtually inactive in ligand exchange processes;[18] therefore the cavities could not bond to the nanoparticle surface. PPh_3-protected nanoparticles, on the other hand, readily exchange with disulfides;[19] their size is smaller than the size of the cavities, which explains their adsorption by the polymer. It is likely that small Au nanoparticles protected by other weakly bound ligands (*e.g.*, thioethers, amines *etc.*) will also be adsorbed by such imprinted polymers.

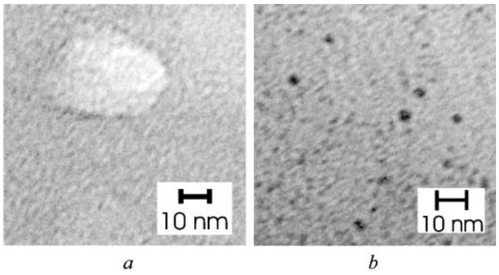


Fig. 5 TEM images of nanoparticle-imprinted polymer before (a) and after (b) treatment with PPh_3-coated Au nanoparticles.

To summarise, we have described a simple procedure for embedding polymerisable Au nanoparticles into macroporous cross-linked polymers. Etching the Au core from these materials results in nanoparticle-imprinted polymers, containing nanometer-sized cavities lined with disulfide functional groups. The polymers are capable of selective sorption of small PPh_3-protected Au nanoparticles. Such smart materials may find applications for selective recognition of nanostructures or as synthetic nanoreactors.

Notes and references

1 M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293; A. C. Templeton, W. P. Wuelfing and R. W. Murray, *Acc. Chem. Res.*, 2000, **33**, 27.
2 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801.
3 X.-M. Li, J. Huskens and D. N. Reinhoudt, *Nanotechnology*, 2003, **14**, 1064; W. Guo, J. J. Li, Y. A. Wang and X. G. Peng, *Chem. Mater.*, 2003, **15**, 3125.
4 A. C. Templeton, M. J. Hostetler, C. T. Kraft and R. W. Murray, *J. Am. Chem. Soc.*, 1998, **120**, 1906.
5 S. M. Marinakos, J. P. Novak, L. C. Brousseau, A. B. House, E. M. Edeki, J. C. Feldhaus and D. L. Feldheim, *J. Am. Chem. Soc.*, 1999, **121**, 8518; S. M. Marinakos, M. F. Anderson, J. A. Ryan, L. D. Martin and D. L. Feldheim, *J. Phys. Chem. B*, 2001, **105**, 8872; L. Sun, R. M. Crooks and V. Chechik, *Chem. Commun.*, 2001, 359; W. Guo, J. J. Li, Y. A. Wang and X. G. Peng, *J. Am. Chem. Soc.*, 2003, **125**, 3901; D. I. Gittins and F. Caruso, *Adv. Mater.*, 2000, **12**, 1947.
6 M. K. Corbierre, N. S. Cameron, M. Sutton, S. G. J. Mochrie, L. B. Lurio, A. Rühm and R. B. Lennox, *J. Am. Chem. Soc.*, 2001, **123**, 10411.
7 A. B. R. Mayer, *Mater. Sci. Eng. C*, 1998, **6**, 155; S. T. Selvan, J. P. Spatz, H.-A. Klok and M. Möller, *Adv. Mater.*, 1998, **10**, 132; J. J. Watkins and T. J. McCarthy, *Chem. Mater.*, 1995, **7**, 1991.
8 J. Matsui, K. Akamatsu, S. Nishiguchi, D. Miyoshi, H. Nawafune, V. K. Tamaki and N. Sugimoto, *Anal. Chem.*, 2004, **76**, 1310.
9 S. Poovarodom, M. M. Y. Chen and A. Katz, *Abstr. Pap. Am. Chem. Soc.*, 2004, **228**, 641-INOR; A. Katz, S. Poovarodom and M. M. Y. Chen, *Abstr. Pap. Am. Chem. Soc.*, 2004, **227**, 442-COLL.
10 S. Koenig and V. Chechik, *Langmuir*, 2003, **19**, 9511.
11 J. F. Ford, T. J. Vickers, C. K. Mann and J. B. Schlenoff, *Langmuir*, 1996, **12**, 1944; M. Niwa, T. Mori and N. Nigashi, *J. Mater. Chem.*, 1992, **2**, 245.
12 P. A. G. Cormack and A. Z. Elorza, *J. Chromatogr., B*, 2004, **804**, 173.
13 M. J. Whitcombe and E. N. Vulfson, *Adv. Mater.*, 2001, **13**, 467–478.
14 W. Wm. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, 1966.
15 R. J. Pudderhatt, *The chemistry of gold*, Elsevier, Amsterdam, 1978.
16 J. Turkevich, P. C. Stevenson and J. Hillier, *Discuss. Faraday Soc.*, 1951, **11**, 55.
17 W. W. Weare, S. M. Reed, M. G. Warner and J. E. Hutchinson, *J. Am. Chem. Soc.*, 2000, **122**, 12890.
18 Y.-S. Shon, C. Mazzitelli and R. W. Murray, *Langmuir*, 2001, **17**, 7735.
19 V. Chechik, H. J. Wellsted, A. Korte, B. C. Gilbert, H. Caldararu, P. Ionita and A. Caragheorgheopol, *Faraday Discuss.*, 2004, **125**, 279.