Recent advances in polymer protected gold nanoparticles: synthesis, properties and applications

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The use of various functionalized polymers as stabilizers to design metal core–organic shell hybrid nanoparticle architectures has attracted increasing interest for different applications. The feature article reviews recent reports published from 2004 to the beginning of 2007 on the synthesis of polymer protected gold nanoparticles (AuNPs), and also comments their properties and applications.

1 Introduction

Nanoparticles, in the 1–100 nm range can be said to bridge the gap between small molecules and bulk materials.[1] As a class of materials, NPs offer a variety of opportunities to investigate the evolution of material properties with particle dimensions. Metal NPs, especially Au, Ag and Cu NPs, have been extensively investigated over the past decade due to their unique electronic, optical and catalytic properties.[2,3] These properties are neither those of bulk metal nor those of molecular compounds as has been widely demonstrated in both experimental and theoretical investigations, but they strongly depend on the particle size, shape and interparticle distance as well as the nature of the protecting organic shell.[4] The chemical stability of NPs is crucial to avoid degradation processes such as partial oxidation or undesired sintering of particles. The lack of sufficient stability of many nanoparticles has impeded the development of real world applications of these nanomaterials. As we have been seeing, gold plays a special role in nanoscience and nanotechnology, due to the fact that[5]

- gold is the most stable noble metal at the nano-scale, so the designers of any nano-device requiring metallic components are likely to favorably consider gold.
- gold is a far better electron conductor than silicon.
- gold offers unique surface chemistry that allows it to be used as a platform on which to self-assemble layers of organic molecules, usually bound to the gold by sulfur atoms.

To date, a number of procedures including physical and chemical methods for synthesis of AuNPs have been reported,[3] of which the most widely used are wet chemistry techniques based on chemical reactions in solution that yield AuNP colloids with a wide range of sizes, shapes and dielectric environments.[6] The most popular method of preparing AuNPs dispersed in water is the reduction of $HAuCl_4$ in a boiling sodium citrate solution.[7,8] The average particle diameter can be tuned over a wide range ($\sim$10–100 nm) by varying the concentration ratio between $HAuCl_4$ and sodium citrate. Another most impressive procedure[9] that has become extremely popular for AuNPs synthesis is the two-phase reduction method developed by Brust and co-workers in the laboratory of Professor David Schiffrin. The paper describing the method has become one of the most cited articles in this field. Alkanethiolate-protected AuNPs (so-called monolayer-protected clusters, MPC) were produced with tunable particle

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sizes between ~1 and 10 nm depending on the ratio of the Au salt and the ligand (alkanethiol). Later on, Murry and co-workers enhanced the popularity of the method and explored routes to functionalized MPCs by ligand place exchange reactions.[4,10] Alkanethiolate MPCs can be repeatedly isolated from and redissolved in common organic solvents without irreversible aggregation or decomposition. The particles can be stored in the solid state under ambient conditions for long term without significant ageing effects. On the other hand, facile one-phase preparation methods in organic solvents such as methanol[11] and tetrahydrofuran[12] of aliphatic and aromatic thiol-functionalized gold and other metal nanoparticles were developed in surfactant-free conditions. Preparation of gold clusters composed of ~10–13 Au atoms (less than 0.8 nm) dispersed in water was reported by Negishi and Tsukuda using a dithiol, meso-2,3-dimercaptosuccinic acid, as a reducing and stabilizing agent.[13]

Recently, the design of core–shell nanoparticle architectures has attracted increasing interest, not only as a means to improve the stability and surface chemistry of the core nanoparticle but also as a way of accessing unique structures, properties and applications *via* combining the different characteristics of the components, which are not obtainable from one nanomaterial alone. The use of polymeric stabilizers for metal nanoparticles has inspired the studies of various synthetic routes to link polymers to metal particles and the investigations on properties as well as potential applications of the hybrid materials. The advantages of using polymers as stabilizers are not only the enhancement of long-term stability, adjustment of the solubility and amphiphilicity of AuNPs, but also the functionalization of AuNPs with polymers to achieve higher and tunable surface-density of shell/brush, and to tailor properties of AuNPs, as well as to promote compatibility and processibility. Though an early report dates back to 1718, where starch was reported to stabilize gold particles dispersed in water,[14] much effort has recently been put to prepare polymer-protected AuNPs (and also other metal particles), in particular, inspired from the two-phase reduction method developed by Brust and co-workers as mentioned above.[9] Various polymers have been reported to protect AuNPs from aggregation, in general, *via* either physisorption or chemisorption on Au nano-cores. The protection of AuNPs through chemisorption where most of the polymers used contain sulfur atoms/groups that possess strong affinities to gold has usually been referred to as covalent binding between sulfur and the Au nano-core as advocated for the case of alkanethiol protected AuNPs. The synthesis routes that have widely been studied toward polymer protected AuNPs *via* covalent binding include the ''grafting to'' and ''grafting from'' techniques, they are the most effective methods that have extensively been reported in the past decade for the synthesis of polymer brushes with high surface density and unique properties on either flat or curved surfaces.[15] In this feature article, we therefore refer to them as the *covalent ''grafting from'' and ''grafting to'' techniques* to be the categories where polymer protected AuNPs are described in combination with living/controlled polymerization techniques, in particular, radical polymerization, such as atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT). On the other hand, the protection of AuNPs with polymers that do not possess specific atoms/groups such as sulfur has been known as *physisorption*, into which the use of water-soluble polymers, block copolymer micelles, star block copolymers, or nanoreactors, is classified. In addition to above categories, many reports were concerned with achievement of core–shell polymer–AuNP hybrids through first preparing AuNPs using small ligands (*e.g.*, alkanethiol and citrate) and then modifying AuNPs with polymers, this approach is classified as *''post-modification of pre-formed AuNPs''*.

This feature article summarizes recent reports on the synthesis of polymer protected AuNPs and their properties and applications, that have been published from 2004 up to the beginning of 2007. Because of the space limitation, we mainly focus on the synthetic routes along the above four categories and comment the properties and applications of AuNPs.

2 Polymer protected AuNPs: synthesis, properties and applications

2.1 Covalent "grafting from" technique

Due to the simplicity and versatility of living/controlled radical polymerization techniques, they have extensively been employed to graft polymer brushes from both planar surfaces and metallic NPs to obtain well-controlled molecular weights of the polymers and well-defined chain architectures.[16–18] The use of the ''grafting from'' technique to prepare polymer brush/shell covered nanoparticles, in particular, combining living polymerization shows several advantages: (1) facile control over the polymer brush thickness upon polymerization conditions such as monomer concentration, temperature and reaction time. (2) The ability to design well-defined polymer architectures such as growing block or comb-coil graft copolymers.[19,20] (3) The ability to control and achieve higher surface graft density of polymer brush by the pre-anchored initiators on the particles surface. The steric hindrance imposed by the grafted polymer chains may be a problem in the case of the ''grafting to'' technique to prepare polymer brush of a high graft density (see subsection 2.1). However, in the ''grafting from'' technique polymer chains grow from the small initiators that have been pre-anchored to the particle surface, and the grafted chains will not hinder the diffusion of the small monomers to the reaction sites, so the polymer brushes with higher graft density can be obtained.[20] (4) The better uniformity of the polymeric films on the surface of various solids. There usually exist three approaches to anchor initiators onto the surface of AuNPs:

- by modification of pre-formed AuNPs on which the protective ligands contain active groups such as hydroxyl, carboxylic acid, glycidyl, *etc.*
- by exchange reaction using new ligands to partially/stoichiometrically substitute the old ones that have already attached on AuNPs. The new ligands are initiators for polymerization.
- by direct attachment of the protective ligands which themselves are capable of initiating polymerization.

Following the first approach, we have synthesized AuNPs using 11-mercapto-1-undecanol as protective ligands and subsequently modified AuNPs into macro-RAFT agents containing dithiobenzoate end groups *via* esterification. Poly(*N*-isopropylacrylamide) (PNIPAM) brush was then grafted from AuNPs *via* RAFT polymerization[21] (Fig. 1). However, one should take into account the possible cleavage of protective ligands from AuNP surfaces under the reaction conditions and the tolerance of the RAFT agents to the basic or acidic media.[22] By the exchange reaction, Kim *et al.*[23] synthesized cross-linked AuNP-PNIPAM core–shell hybrid structures as well as a brush-type AuNP/PNIPAM hybrid through surface-initiated ATRP in aqueous medium. The disulfide initiators, $[BrC(CH_3)_2COO(CH_2)_{11}S]_2$, were bound to AuNPs synthesized by citrate reduction. They studied the effect of cross-linking on the thermo-responsiveness of the AuNP/PNIPAM hybrids for potential use as a stimuli-responsive optical device, such as surface plasmon resonance-based sensing materials. Using the similar method, Li *et al.*[24] prepared core–shell AuNPs and a slightly cross-linked PNIPAM hybrid. Such hybrids can be used to trap and encapsulate other nanoparticles, biomolecules, dyes, or drugs by a temperature-introduced "breathing" process. They also fabricated pH-responsive nanocomposites of AuNPs and poly(4-vinylpyridine) (P4VP) to be used as smart supports to entrap transition metal ions. The ions were reduced *in situ* to construct novel bimetallic nanocomposites, which were regarded as intelligent catalysts with activity regulated by environmental stimuli.[25] Kotal *et al.*[19] synthesized AuNP-poly(methyl methacrylate) (PMMA) core–shell NPs by surface-confined ATRP at elevated temperature. AuNPs were first prepared using 11-mercapto-1-undecanol as protective ligands and then place exchanged with 3-mercaptopropyltrimethoxysilane, followed by hydrolysis and condensation to make a crosslinked silica-primer layer. This cross-linking process solved the problem of thiol ligands detachment from AuNPs surface and enhanced the stability of the monolayer before ATRP was conducted.

Use of DNA– and protein–nanoparticle bioconjugates has attracted a great interest in constructing programmed nanostructures, such as one-dimensional nanowires and two-dimensional nanoarrays, for applications in nanoelectronics, optoelectronics, biosensing and biodiagnostics.[26,27] DNA was chosen as a polymer material mainly due to the specificity of DNA base-pairing, the predictability of inter- or intramolecular interactions, its physicochemical stability and mechanical rigidity. In addition, DNA can be manipulated and modified by a wide range of enzymes, including DNA polymerase, ligase and restriction endonucleases. The powerful, convenient and specific enzymatic manipulations make DNA a highly desirable building block for the construction of various nanostructures.[28] Zhao *et al.*[28] demonstrated that long single-stranded DNA can be grafted directly from AuNP surface with applying rolling circle amplification (RCA) reaction, catalyzed by a special DNA polymerase known as ϕ29 DNA. AuNPs of 15 nm diameter were first prepared by the classical citrate reduction route. Thiol-modified DNA primers (41 nucleotides) were then attached onto the nanoparticles. A 63-nucleotide-long circular DNA template was then annealed with the DNA-functionalized AuNPs. The resultant DNA–AuNP assemblies can be further used as a unique scaffold (Fig. 2). Higuchi *et al.*[29] have recently prepared peptide–AuNPs by the "grafting from" technique. The peptide chains grew by ring-opening polymerization of γ-methyl-L-glutamate *N*-carboxyanhydride with fixed amino groups on the nanoparticle surface as initiators. The number of peptide chains on the surface was adjusted to *ca.* two molecules per gold nanoparticle by controlling the number of amino groups on the surface. The surface peptide chains were in an α-helical conformation and AuNPs formed a fibril assembly owing to the dipole–dipole interaction between the surface peptide chains.

Microcontact printing technique has been popular for the routine fabrication of large-area arrays of patterned self-assembled monolayers on 2D bulky surfaces, such as gold and silica surfaces, since developed by Kumar and Whitesides.[30] Micropatterned polymer brushes have shown promise as components in micro-electronics, cell-growth regulation, biosensors, microreaction vessels and drug delivery.[31] Jung *et al.*[32] fabricated micropatterned AuNP arrays that served as templates from which to graft PNIPAM brushes *via* the surface-initiated ATRP. AuNPs used for micropatterning were

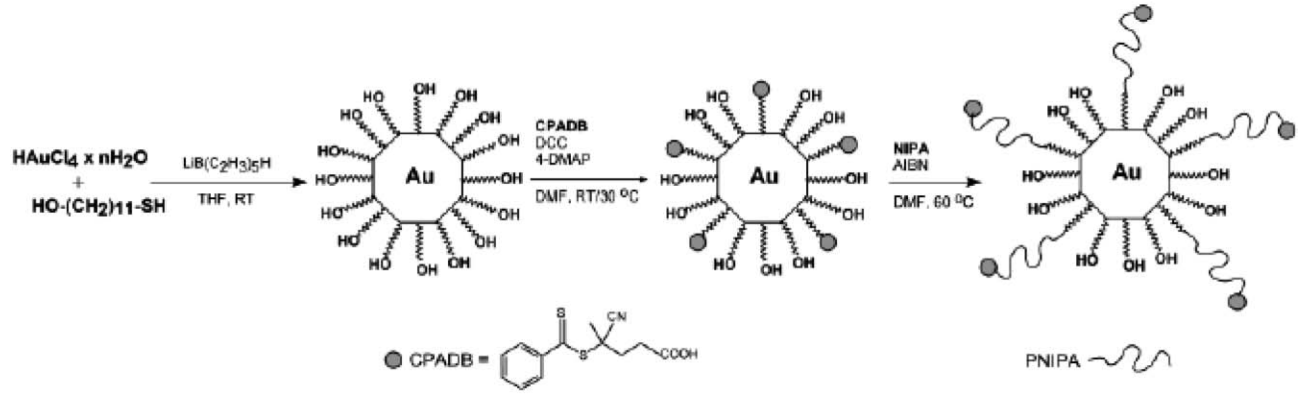

Fig. 1 The synthetic steps for PNIPAM–AuNPs by the covalent "grafting from" technique, through the modification of pre-formed AuNPs into macro-RAFT agents containing dithiobenzoate, followed by RAFT polymerization. (Reproduced with permission from ref. 21. Copyright 2003, American Chemistry Society.)

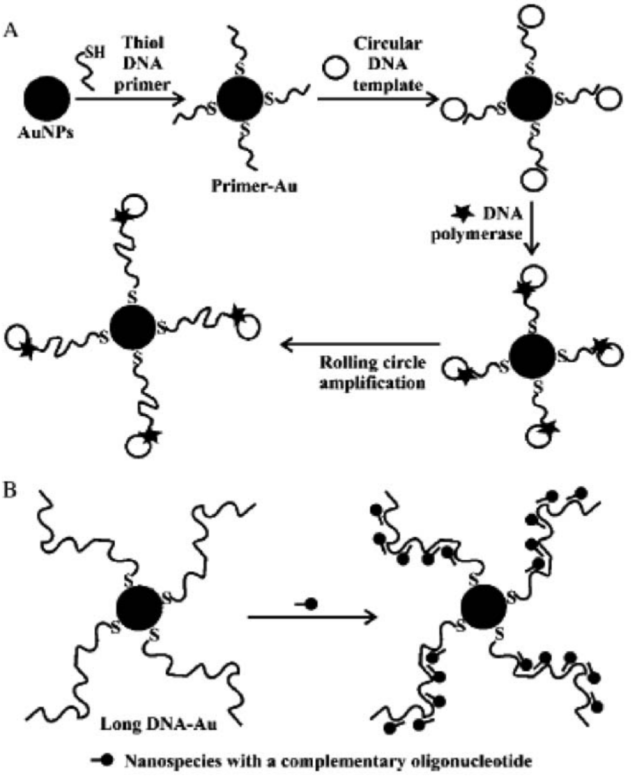

Fig. 2 (A) Schematic illustration of DNA polymerization from AuNPs *via* RCA. (B) DNA–AuNP conjugates as scaffolds for the formation of 3D nanostructures. (Reproduced with permission from ref. 28. Copyright 2006, Wiley.)

prepared by reducing $HAuCl_4$ with sodium citrate. The thiol initiators, $BrC(CH_3)_2COO(CH_2)_{11}SH$, were then bound onto AuNPs for ATRP. The polymer brush underwent a phase transition triggered by external stimulus. This reversible phase transition of micropatterned nanoparticles has significant promise for achieving control in tissue engineering and for biosensor applications.

2.2 Covalent "grafting to" technique

AuNPs protected with polymers can be prepared directly and facilely by the covalent "grafting to" technique without tedious synthesis and purification which are often required in the covalent "grafting from" technique. Much effort on one-pot synthesis of AuNPs has been reported in the last decade using sulfur-containing polymers which bear functional groups such as *dithioester*, *trithioester*, *thiol*, *thioether* and *disulfide* at one end of a polymer chain or in the middle. In this subsection, we describe AuNP syntheses following this sequence of using sulfur-containing polymers. The resulting AuNPs can be seen as analogues of alkanethiol protected AuNPs synthesized *via* the two-phase method.[9] They are very stable in solid state over years without perceivable size aging and can be repeatedly dissolved. Another marked advantage by the covalent "grafting to" technique is the possibility to achieve a high surface graft density of polymer brush on AuNP surface. Corbierre *et al.*[33] synthesized AuNPs protected with either tetradecanethiol (C_{14}–SH) or thiolated polymers (polystyrene, PS–SH and poly(ethylene oxide), PEO–SH) with different molar masses by a covalent "grafting to" technique. They compared the surface density of the small ligand to those of the polymer ligands, also in contrast with the surface densities of the same protective species self-assembled onto a flat gold surface. The surface densities of the small ligand on either AuNP or flat gold surfaces are higher than those of polymer ligands. Increasing the chain length leads to an increase in the steric hindrance of ligands, resulting in decreasing the corresponding surface density both on AuNP and flat gold surfaces. However, it is significant that the surface densities of polymeric ligands on AuNPs are 1.2- to 23.5-fold greater than those on flat gold surfaces. The authors concluded that the presence of the voids at the facet edges (assuming that Au nano-cores adopt truncated octahedral structure) provides extra volume for grafting the polymeric ligands (Fig. 3), and presented a graph of the percentage of void volume as a function of the core radius with various brush thicknesses (Fig. 4). We collected the surface densities of both small and polymer ligands on AuNP surfaces published in recent years

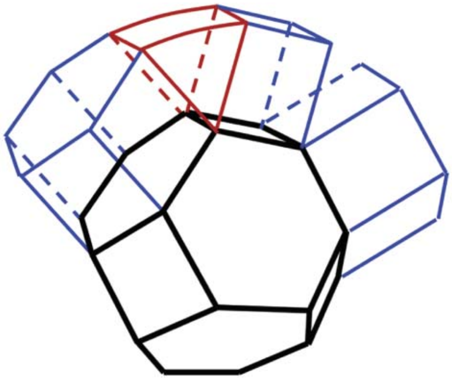

Fig. 3 Representation of a void volume (red) between two polymer brushes (blue) adsorbed on a gold nano-core (black). (Reproduced with permission from ref. 33. Copyright 2004, American Chemical Society.)

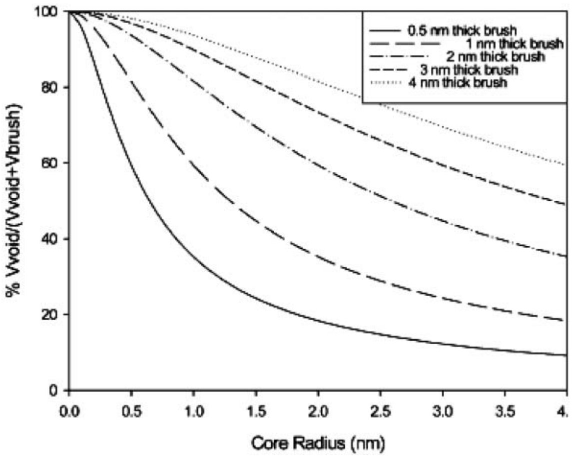

Fig. 4 Graph of the calculated percentage of void volume compared to the volume of the void plus the volume of the brush, as a function of the core radius (nm), for various brush thickness. (Reproduced with permission from ref. 33. Copyright 2004, American Chemical Society.)

Table 1 Surface graft densities of some alkanethiols and polymer brushes on AuNPs

AuNP	Ligand M_n/g mol^{-1}	Diam. Au core/nm	Density/chain nm^{-2}	Footprint/nm^2 chain^{-1}	Ref.
C12S–AuNPs	202.40	2.8	4.76	0.21	34
C12S–AuNPs	202.40	5.2	4.76	0.21	9
C14S–AuNPs	230.45	3.9 ± 0.5	4.35	0.23	33
PNIPAM–AuNPs	4700	2.0 ± 0.8	2.5	0.40	35
PNIPAM–AuNPs	4700	2.2 ± 0.8	2.2	0.45	35
PNIPAM–AuNrPs	5400	1.5 ± 0.5	2.4	0.42	35
PNIPAM–AuNPs	5400	2.3 ± 0.8	1.8	0.54	35
PS–AuNPs	3400	2.05	1.64	0.61	36
PS–AuNPs	3400	2.54	1.45	0.69	36
PS–AuNPs	3400	2.68	1.12	0.89	36
PS–AuNPs	3400	2.76	0.83	1.20	36
PS–AuNPs	3400	3.46	0.75	1.33	36
PS–AuNPs	3400	5.11	0.32	3.13	36
PS–AuNPs	2000	4.4 ± 1.2	3.45	0.29	33
PS–AuNPs	13300	6.2 ± 1.7	0.94	1.06	33
PEO–AuNPs	2100	3.6 ± 2.0	1.15	0.87	33
PEO–AuNPs	2100	3.8 ± 1.9	0.98	1.02	33
PEO–AuNPs	5000	2.8	2.86	0.35	34

synthesized by the covalent "grafting to" technique, and show them in Table 1.

We have studied the synthesis methods of AuNPs protected with a thermo-responsive PNIPAM by the covalent "grafting to" technique with different end-functional PNIPAMs and various ratios between PNIPAM and $HAuCl_4$.[35] PNIPAM samples were synthesized through either conventional radical polymerization or living/controlled radical polymerization (*i.e.*, RAFT). In the former case, PNIPAM had to be modified into thiol end-capped polymer, but the modification efficiency was not high and the resulting AuNPs protected with this type of PNIPAM tended to cross-link into a network. On the other hand, either by directly using RAFT-PNIPAMs synthesized through RAFT polymerization that contain dithioester (dithiobenzoate) as an end group (a one-pot reaction) or by using thiolated PNIPAM obtained *via* hydrolysis of RAFT-PNIPAM, the AuNPs protected with PNIPAM, PNIPAM–AuNPs, were successfully prepared (Fig. 5).[35,37] We believe that in the course of synthesis the reductant used, $LiB(C_2H_5)_3H$, can reduce $HAuCl_4$ to Au(0) and also simultaneously hydrolyzes the dithioester end group to a thiol which immediately protects AuNPs.[38] All prepared AuNPs were analyzed by high-resolution transmission electron microscopy, HRTEM, thermo-gravimetric analysis, TGA, dynamic light scattering, DLS, NMR, UV-vis and FTIR. The characteristics of AuNPs such as particle and gold core sizes, formulas of particles, PNIPAM shell thickness in water, and the surface density and footprint of PNIPAM brush were thus determined.

We investigated the thermal properties of PNIPAM–AuNPs dispersed in water by high sensitivity microcalorimetry. AuNPs were synthesized by the "grafting to" technique and were protected by short PNIPAM chains of *ca.* 5000 g mol^{-1}.[39] What we observed was two separate phase transitions of the PNIPAM brush, different from that of corresponding free PNIPAM dissolved in water (Fig. 6). Further studies on

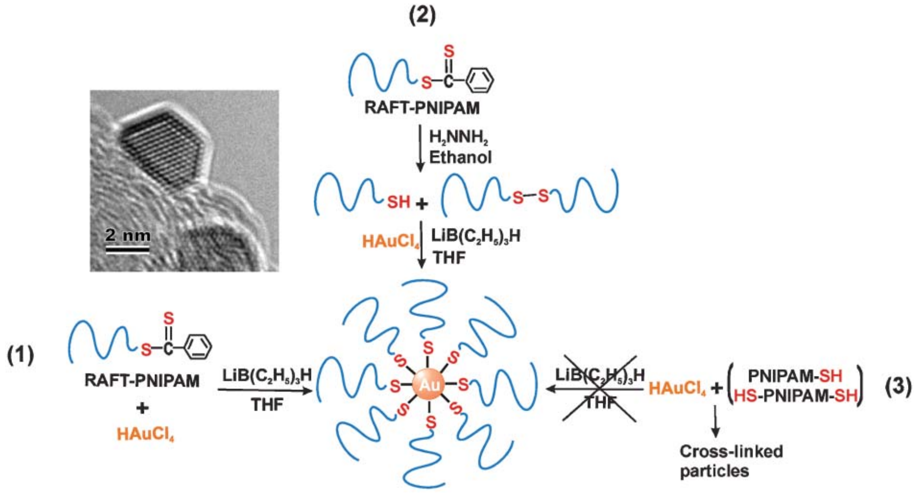

Fig. 5 The synthetic routes for PNIPAM–AuNPs by the covalent "grafting to" technique. (1) One-pot reaction through directly dissolving RAFT-PNIPAM and $HAuCl_4$ in THF. (2) Pre-hydrolysis of RAFT-PNIPAM into thiolated polymer. (3) Modification of PNIPAM synthesized *via* conventional free radical polymerization into a thiolated polymer. Inset is a HRTEM image of PNIPAM–AuNPs synthesized *via* one-pot reaction. Adapted with permission from ref. 37.

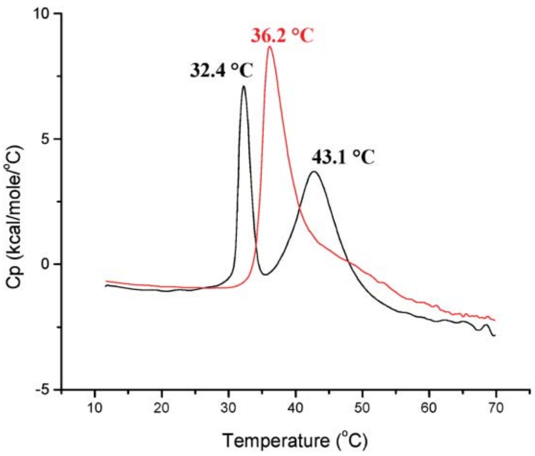

Fig. 6 Microcalorimetric endotherms for aqueous solutions of PNIPAM–AuNPs (black line, 0.16 mmol L^{-1} of PNIPAM brush) and corresponding free PNIPAM dissolved in water (red line, 0.18 mmol L^{-1} of free PNIPAM). The peak temperatures are shown close to the corresponding peaks. (Adapted with permission from ref. 39. Copyright 2004, American Chemical Society.)

the concentration dependence of the two phase transitions of PNIPAM brush received an insight of how the PNIPAM chains interact in the outer shell and cooperate in the inner shell during the course of the phase transition. We assumed that the interchain cooperativity taking place in the inner shell may be very much dependent on the surface density of the polymer brush. We tentatively put forth a model of the structure of the PNIPAM brush. Liu and co-workers[40,41] later observed a similar phenomenon, *i.e.*, a double phase transition of the PNIPAM shell grafted from a hydrophobic dendritic core.

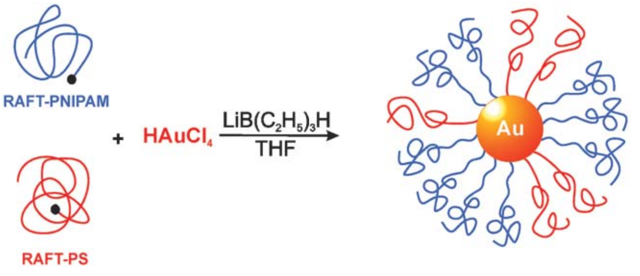

Fig. 7 The synthesis and structure of amphiphilic AuNPs by the covalent "grafting-to" technique. (Adapted with permission from ref. 42, also see ref. 37. Copyright 2005, American Chemical Society.)

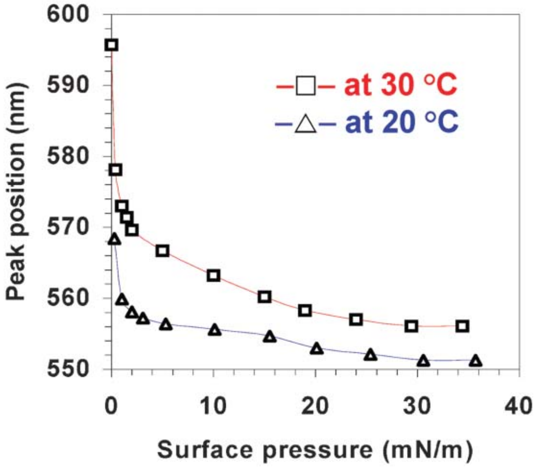

Fig. 8 The peak position of in situ SPR band as a function of surface pressure for the amphiphilic AuNP monolayers compressed at 20 and 30 °C, respectively. (Adapted with permission from ref. 43. Copyright 2006, American Chemical Society.)

We also synthesized amphiphilic AuNPs protected with a mixture of PS and PNIPAM chains in a one-pot reaction by the "grafting to" technique (Fig. 7).[42,43] The amphiphilicity of the AuNPs can be tuned either by varying the feed ratio between PS and PNIPAM in the synthesis or by changing the relative chain lengths of the polymers. Monolayers of the amphiphilic AuNPs at the air/water interface at different temperatures were built up by employing a Langmuir trough. This enabled the *in situ* investigation of the optical properties of the monolayers. During the compression of the monolayer the conformations of the PNIPAM chains change, this affecting the optical properties. It is well-known that noble metal NPs exhibit a strong absorption band in the visible light region, *i.e.*, a surface plasmon resonance (SPR) band, this being a characteristic of small nanoscaled particles. The assembling of these NPs into two and three-dimensional ordered macrostructures offers a special pathway for the design of materials that have potential applications in optical and microelectronic devices,[44] chemical and biosensor technology,[45] *etc.* Langmuir trough enables a very high degree of control over the layer density and particle ordering, since the monolayer at the interface can be manipulated by compressing to a desired surface pressure prior to the transfer of the monolayer on a substrate. We observed that the SPR band of AuNP monolayer significantly shifts to a shorter wavelength during the initial increase of the surface pressure (*i.e.*, a blue shift), and with a further rise in the surface pressure, the blue shift gets more gradual (Fig. 8).[43] Taking into account the coupling effect between adjacent particles based on the interparticle distance of $d/2r$ (d is the center-to-center distance between adjacent gold cores and $2r$ is the diameter of the gold core),[46] we concluded that the blue shift of the in situ SPR was

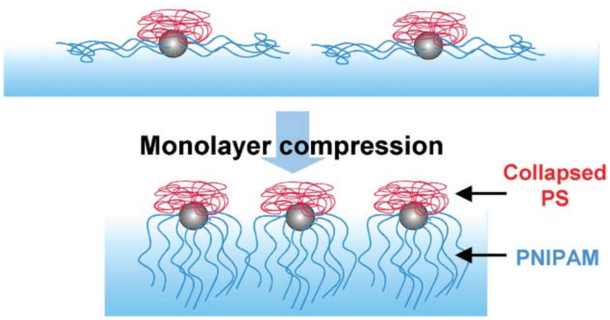

Fig. 9 Schematic representation of the conformational change of tethered PNIPAM chains (blue ones) from a flattened and stretched structure at the air/water surface to a brush-like structure in the water subphase upon the monolayer compression. The collapsed PS chains are red. (Reproduced with permission from ref. 43. Copyright 2006, American Chemical Society).

compression-induced and closely related to the conformational change of the PNIPAM chains. The conformational change of the PNIPAM, as demonstrated in Fig. 9, may result in a decrease in the polarity of the local environment of the gold core, leading to a notable blue shift. Our observation was in contradiction to the earlier reports for alkanethiol protected Ag[46] and AuNPs,[47] where a significant red shift was observed due to the coupling effect of adjacent particles. To conclude, the use of the thermo-responsive amphiphilic AuNPs to make a film using Langmuir trough provides a way to tune optical properties of the NP film by not only surface pressure but also by temperature.

Suzuki and Kawaguchi[48] demonstrated a synthesis of AuNPs using thermosensitive core–shell particles as templates and $NaBH_4$ as a reducing agent. The template core–shell particles, with cores composed mainly of poly(glycidyl methacrylate) (PGMA) and shells composed mainly of PNIPAM, were functionalized with either thiols or amines. When amino-functionalized particles were used as templates, the obtained AuNPs were as stable as thiol-functionalized ones, but they flocculated with heating. In contrast, the thiol groups are more effective for holding the AuNPs inside the shell for long-term storage and applications. The hybrid particles exhibited a reversible color change, which originated from SPR of AuNPs and was temperature-dependent in the range of 25–40 °C, and they have potential applications in sensors and photonic or electronic devices.

Trithioester-containing polymers can also chemically adsorb onto AuNPs and further protect AuNPs. These polymers are easily synthesized by RAFT polymerization with trithiocarbonate as the chain-transfer agent. Fustin *et al.*[49] reported a simple procedure to tune the hydrophilicity of the pre-formed hybrid AuNPs by directly adding hydrophilic trithiocarbonate-containing poly(acrylic acid) (PAA) chains to AuNPs. The AuNPs were successfully transferred from organic solvent to water. The hybrid AuNPs were prepared in the core of a poly(ethylene glycol)-*b*-poly(ε-caprolactone) (PEG-*b*-PCL) five-arm star block copolymer in an organic solvent.[50]

Incorporation of nanoparticles into polymer matrices to form nanocomposites is of particular interest for materials engineering and significantly impacts on a wide range of material properties, including mechanical strength, permeability, catalytic activity, conductivity and optical properties.[51] These properties, however, generally depend on how the particles are dispersed within the polymer matrix. A desirable approach involving the incorporation of pre-made nanoparticles into pre-synthesized polymer with the use of a common solvent has been recently reported,[52–54] that provides full synthetic control over both the nanoparticles and the matrix. To make nanoparticles well-dispersed in a polymer matrix, chemical matching between the polymer protecting the nanoparticles and the host polymer matrix is a prerequisite. Actually, other factors also govern the compatibility between a polymer brush and a polymer matrix. Brush wetting or de-wetting by a polymer matrix (that leading to nanophase separation of the composite and aggregation) is known to be a function of the brush grafting density, the molecular weights of both the polymer brush chains and the matrix polymers, as well as the presence of additional solvent.[55] Corbierre *et al.*[33,55] have demonstrated how the combination of these factors, in addition to the geometry of the gold core, leads either to dispersion, partial aggregation, or complete aggregation of polymer-protected AuNPs in a matrix of the same polymer species. AuNPs protected with thiol-terminated polymers, PS-SH or PEO-SH, of various molecular weights were synthesized respectively *via* the "grafting to" technique. The dispersion of PS–AuNPs in PS matrices and PEO–AuNPs in PEO matrices was studied. It was pointed out that the faceted three-dimensional surface of gold core appears to be a rather unique surface on which to form polymer brushes, and a brush-matrix phase diagram involving faceted nanoparticles was distinct from two-dimensional and spherical three-dimensional cases. The presence of a large volume fraction of voids in the brush, due to the truncated octahedral geometry of the gold core, apparently increased the matrix-nanoparticle compatibility (see Fig. 3).

Block copolymers consisting of chemically different blocks can hierarchically self-assemble into a diversity of polymeric structures at a length scale of 10–100 nm, such as the lamellar (1D), cylindrical (2D), spherical and gyroid (3D) phases.[56] This offers an efficient route for bottom-up construction of nanostructures of nanoparticles based on polymeric self-assembly. Thus, incorporation of nanoparticles into block copolymers has recently been explored for the fabrication of novel functional materials such as nanostructured solar cells, photonic band-gap materials, and highly efficient catalysts.[57] Chiu *et al.*[58] investigated the localization of PS, poly(2-vinyl pyridine) (P2VP) and PS/P2VP-protected AuNPs in a PS-*b*-P2VP lamellar diblock copolymer phase. All the AuNPs were synthesized utilizing thiol-terminated PS and P2VP *via* the "grafting to" technique. They demonstrated precise control of the location of the particles within the matrix simply by varying the number of polymer ligands on the particle surfaces. AuNPs protected with a mixture of PS and P2VP adsorbed at the interfaces between the PS and P2VP blocks, while AuNPs protected with only PS or P2VP segregated near the center of the compatible domain. Kim *et al.*[36] further described the effect of the grafting density of PS chains bound to gold cores on the particle location within a PS-*b*-P2VP lamellar diblock copolymer phase. The PS grafting density on gold cores was varied by changing the initial feed ratio of PS-SH chains to gold atoms through the "grafting to" technique. It was found that the grafting density of PS chains on AuNPs was critical to controlling their location in block copolymer templates. PS-protected AuNPs with PS grafting density >1.6 chains nm^{-2} were dispersed in PS domains of PS-*b*-P2VP, while they segregated along the interface between PS and P2VP domains of PS-*b*-P2VP for PS grafting density <1.3 chains nm^{-2}. However, no such grafting density effect was observed for P2VP protected AuNPs, demonstrating that there is a preferential interaction between the P2VP block and the AuNP surface less shielded by PS.

The development of a practical approach for assembling inorganic nanoparticles into well-defined arrays is crucial in the realization of technologically useful inorganic nanoparticle-based materials, but still remains challenging. Many techniques reported towards this approach were based on the biomolecular templates.[59,60] Biomacromolecules such as DNA and proteins have been used as linker molecules for the programmed assembly of AuNPs. In those reports, AuNPs were pre-formed and then mixed with the linker molecules. However, Bhattacharya *et al.*[61] illustrated a simple one-step process where proteins can act as templates when present in solution during the synthesis of AuNPs. The proteins directed the assembling of AuNPs into a 3D, rod-like fashion when cooled to −20 °C followed by thawing at room temperature (Fig. 10). The proteins reported were antibodies to vascular endothelial growth factor 165 isoform (VEGF), epidermal growth factor receptor (C225), immunoglobulin G (IgG), and bovine serum albumin (BSA). The formation of a self-assembled structure in the form of a continuous rod, or the assembly of discrete nanoparticles in a rod-like fashion, can be tailored by controlling the ratio of the precursor $HAuCl_4$ to the antibody/protein used as the template. It was also found that the templating effect of the proteins was absent when the proteins were added to pre-formed solutions of AuNPs. Association of the protein with $HAuCl_4$ before the reduction therefore was essential for this antibody-mediated self-assembly. It was important that the assembled structure was obtained only after freezing to a subzero temperature followed by thawing. Freezing might facilitate the assembly by reducing the Brownian motion of AuNPs, thereby decreasing the electrostatic barrier, and increasing the hydrophobic interactions owing to the presence of proteins. It was well recognized that the attachment of AuNPs with proteins basically depends on three factors: (i) the initial association of the negatively charged AuNPs with positively charged protein takes place because of electrostatic interactions; (ii) after entering into the action radius of the proteins, a covalent interaction between the gold and protein takes place, owing to the presence of thiols/amines in the cysteine and lysine residues in the proteins; and (iii) hydrophobic interactions. As suggested, these types of AuNP–antibody nano-bioconjugates may not only have interesting physicochemical and optoelectronic properties, but may also have intriguing biological properties due to the presence of the antibody. Since the VEGF antibody is a well-established anti-angiogenic substance for clinical use in human diseases, these nano-bioconjugates might find interesting applications in angiogenesis-dependent disorders, such as arthritis, psoriasis, diabetic retinopathy and cancer.

The excellent biocompatibility and biodegradability of poly(ε-caprolactone), PCL, make it well suited for drug/gene delivery and tissue engineering,[62] however, their fate *in vivo* cannot be directly observed by TEM in a histological section. The labeling of PCL biocarrier by a contrasting agent such as AuNPs is thus highly desirable. Aryal *et al.*[63] synthesized PCL terminated by 2-(2,4-dinitrophenylsulfanyl)ethanol *via* ring opening bulk polymerization of ε-caprolactone, followed by removal of the protecting group to obtain thiol end capped PCL (PCL-SH). The PCL-SH chains were grafted to AuNPs by direct incorporation following the Brust–Schiffrin method. The labeled PCL nanocarrier is potential in the application of biospecific labeling of tissues.

Conjugated polymers have been widely studied for the fabrication of polymeric light-emitting diodes (PLEDs). Of π-conjugated polymers, polyfluorene (PF) and its derivatives have enjoyed great attention, mainly because of their high photoluminescence properties and device efficiencies, and their good thermal stability and solubility.[64] Introducing aryl co-monomers such as thiophene into PFs could enhance the spectral stability and electroluminescence efficiency. It has been reported that doping of metal NPs into light-emitting polymers enhances the luminescence properties because of the quenching of triplet excitons whose energy levels overlap with the absorption bands of metal NPs.[65] However, metal NPs are often coated with dispersing agents such as alkanethiols or polymers. These additional non-conjugated dispersing agents increase the electrical resistance and the threshold voltage of devices fabricated with such composite materials. To eliminate the use of any dispersing agents by directly capping 10–20 nm AuNPs at the ends of a conjugated copolymer for enhancing

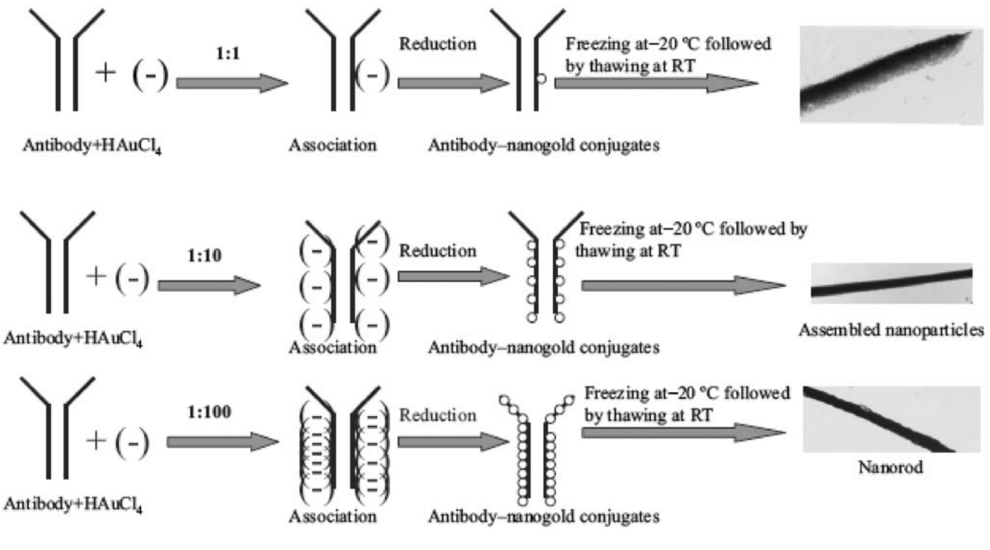

Fig. 10 Interaction of $HAuCl_4$ with a vascular endothelial growth factor-165 isoform (VEGF) antibody, which ultimately leads to the formation of an organized structure. (Reproduced with permission from ref. 61. Copyright 2006, Wiley.)

the performance of a device, Wu *et al.*[66] synthesized an alternating copolymer of poly(9,9-dioctylfluorene-*alt*-thiophene) (PDOFT) terminated with thiol and investigated a green polymeric light-emitting diode material of PDOFT–AuNPs prepared by the "grafting to" technique. The enhanced performance of the PDOFT–AuNP devices and inherent high conductivity (due to AuNPs) showed PDOFT–AuNPs to be not only excellent candidates for a green-light-emitting material, but also to be applied to other electrical devices, such as organic thin-film transistors.

Synthesis of monodisperse metal NPs has always been challenging. Hussain *et al.*[67] recently reported a single-step method which leads to near monodisperse AuNPs in the size range of 1–4 nm in the presence of a water-soluble dodecylthioether end-functionalized poly(methacrylic acid) (PMAA) stabilizer. The particle size was controlled precisely by the ratio of Au to stabilizer and the particles were readily obtainable in both aqueous and nonaqueous solutions. The cause of low polydispersity in AuNPs was not well understood, but the possibility that the clusters were pre-organized within monodisperse micelles formed by the polymer was ruled out by determining the critical micelle concentration of the polymer, which was well above the concentrations used in the majority of the experiments. Thus, this simple protocol for the gram-scale preparation of monodisperse AuNPs below 5 nm would be of practical value for numerous applications when monodispersity is required.

Huang *et al.*[68] synthesized a methylstyrenic polymer containing thioether side groups, PMS–$(CH_2SCH_3)_n$, which afforded many chemisorption sites per molecule to AuNPs. AuNPs were synthesized by the "grafting to" technique with varying the PMS–$(CH_2SCH_3)_n$/$HAuCl_4$ ratio. Although PMS–$(CH_2SCH_3)_n$–AuNPs were relatively stable below the T_g of PMS ($\sim$102 °C), the AuNPs were free to remove and started aggregation at temperatures above the T_g. The presence of AuNPs enhanced significantly the decomposition of polymer ascribed to the quantum size effect of AuNPs.[69] Wan *et al.*[70] described a synthesis of a thioether-containing amphiphilic hyperbranched polyglycerol polymers and their application in the synthesis of AuNPs by the "grafting to" technique.

Higashi *et al.*[71] described the preparation of polypeptide (poly(γ-benzyl-L-glutamate)) monolayer-covered AuNPs through a terminal disulfide S–S bond in polymer by the two-phase method.[9] The polypeptide chains grafted to the surface of gold cluster were found to stretch away and favored to adopt an α-helix conformation with nearly a 100% helix content. The enhancement in helicity was due to the assembled structure of the polypeptide chains. Azzam and Eisenberg[72] synthesized a series of AuNPs protected with biodegradable and biocompatible PEO-*b*-PCL by the "grafting to" technique. PEO-*b*-PCL block copolymer modified with a disulfide moiety in the terminal position of the hydrophobic PCL block was prepared and used as the ligand for the formation of stabilized AuNPs. The AuNPs were used to form soluble micelles in water that showed a core–shell structure with one gold core per micelle. These have a potential for drug delivery in conjunction with tissue and subcellular localization studies.

2.3 Post-modification of pre-formed AuNPs

In many applications, monodisperse fractions of metallic nanoparticles are required, such as in electrochemical quantized capacitance charging[73] and single-electron transistor assembly,[74] *etc.* By the "grafting to" technique, AuNPs are very simply synthesized and directly protected with polymers, but they usually have a broad distribution of the size of the gold cores (the deviation over 20%). As the tethered polymer chains are quite large, they may bring a trouble with further fractionation of AuNPs. However, the post-modification of pre-formed AuNPs to prepare polymer protected AuNPs can circumvent the above drawback. Here the pre-formed AuNPs are usually obtained through citrate reduction[7,8] or the two-phase method using alkanethiols as protective ligands.[9] Thus, the benefits of this way are twofold. The first one is significant, that is, the pre-formed AuNPs may be fractionated according to the size of the gold cores to gain very monodisperse particles (the deviation usually <5%). The second benefit is that the pre-formed AuNPs offer surfaces on which to realize either a facile exchange of weakly bound surface citrate ions with polymer grafts or modification of end-functionalized alkanethiols with polymers.

Kang and Taton[75] reported the preparation of core–shell AuNPs *via* the block copolymer self-assembly approach. Hydrophobic modification of citrate-capped AuNPs with 1-dodecanethiol was made first. These hydrophobic AuNPs were then dispersed in a good solvent (DMF) in the presence of a block copolymer PS-*b*-PAA. Addition of water, which is a nonsolvent for both PS block and 1-dodecanthiol stabilized AuNPs, induced micellization of PS-*b*-PAA around each single hydrophobically functionalized AuNP and resulted in the formation of hybrid core–shell AuNPs. Subsequent cross-linking of the PAA corona can permanently fix the core–shell nanostructure. This approach showed a benefit of no need for ligand chemistry between AuNPs and block copolymers, instead, any nanomaterials with hydrophobic surface functionalities can be encapsulated inside micellar cores. However, by this approach also cross-linked block copolymer micelles without capsulated AuNPs were formed which led to tedious separation. In fact, this approach concerns either the adsorption of polymers on a substrate or the incorporation of molecular solutes into polymer micellar cores, very much dependent upon the radius of curvature of substrate to the radius of gyration of the polymer (ρ/R_g).[76] Kang and Taton[77] further investigated the structure of the cross-linked PS-*b*-PAA shells that was determined by the initial interaction between the copolymer and the nanoparticle surface (Fig. 11). In the case of AuNPs smaller than 10 nm, for which particle size was comparable to the dimension of the block copolymer ($\rho_{Au}/R_g \approx 1$), AuNPs acted like solutes that were dissolved within PS-*b*-PAA micelle cores. Whereas for AuNPs larger than 10 nm ($\rho_{Au}/R_g > 1$), PS-*b*-PAA adsorption was templated by the AuNP surface, and a concentric core–shell structure was formed. The thickness of this shell can be predicted from theoretical models of polymer adsorption onto highly curved surfaces and controlled by varying the ratio of polymer to available nanoparticle surface area. As a result, these rules illustrated how cross-linked copolymer shells with

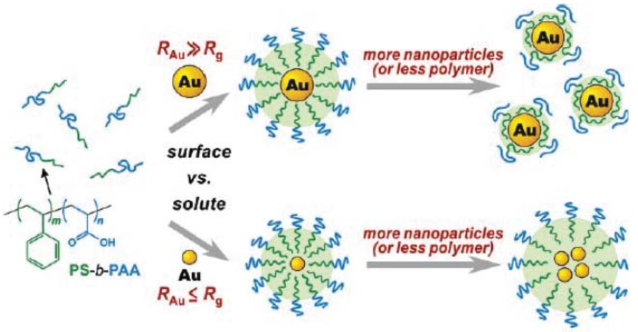

Fig. 11 Schematic representation of PS-*b*-PAA adsorption to large AuNPs, and small AuNPs as solutes to dissolve within PS-*b*-PAA micelle cores. (Reproduced with permission from ref. 77. Copyright 2005, American Chemical Society.)

predetermined thickness can be used to stabilize and functionalize a variety of nanoparticle materials. Luo *et al.*[78] synthesized hybrid core–shell AuNPs by using double hydrophilic block copolymer poly(2-(dimethylamino)ethyl methacrylate)-*b*-poly(ethylene oxide), PDMA-*b*-PEO, with a thiol group end-capped to the PDMA block, to graft to citrate-capped AuNPs. Thiol end-capped PDMA-*b*-PEO was synthesized *via* a RAFT reaction followed by hydrolysis. The inner shell of PDMA close to the gold core was cross-linked to enhance the colloidal stability. These hybrid core–shell AuNPs before cross-linking only weakly aggregated when heating up to the lower critical solution temperature (LCST) 35 °C of PDMA block at pH = 9, due to the protection of hydrophilic PEO block at the outer corona. However, the cross-linking of the hybrid AuNPs leads to a permanent core–shell nanostructure with much higher colloidal stability.

Metal nanostructures may have useful effects on the photoluminescence of nearby emitters. It has been found that chromophores situated in the vicinity of isolated colloidal metal particles in suspension usually experience quenching of their fluorescence,[79,80] Schneider and Decher[80] fabricated metal core–polymer shell capsules by use of layer-by-layer (LBL) deposition of oppositely charged polyelectrolytes onto 13-nm-diameter AuNPs, where nonfluorescent polyelectrolytes are spacer layers and fluorescent organic dyes are situated in the outer polymer layer (Fig. 12). AuNPs were synthesized using the reduction of $HAuCl_4$ by trisodium citrate. Photophysical investigations revealed strongly distance-dependent fluorescence quenching in the core–shell nanoparticles. The contribution of the metal core to this quenching can be assessed precisely after the gentle dissolution of the gold cores by potassium cyanide. The fluorescently labeled core–shell particles may have potential applications in diagnostic or sensing devices.

The combination of biomacromolecules to NPs can provide interesting tools for mimicking the biomolecules present in cellular systems, probing the mechanisms of biological processes, as well as developing chemical means for the handling and manipulating biological components.[81] The labeling of target biomolecules with AuNPs has revolutionized the visualization of cellular and/or tissue components by

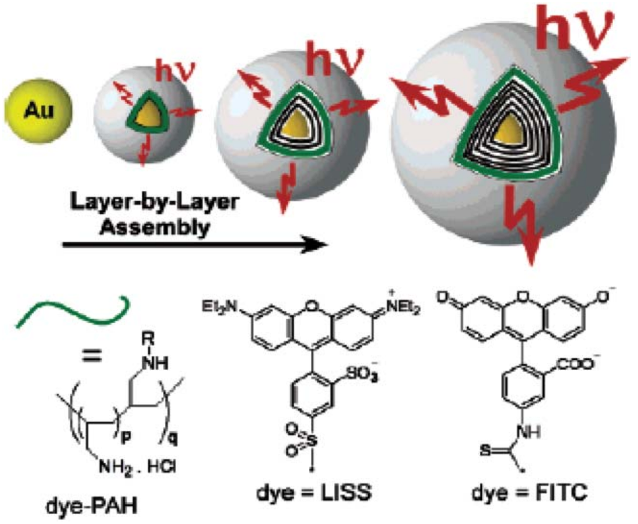

Fig. 12 Layer-by-layer assembly for the construction of core–shell nanoparticles containing fluorescent corona layers. The fluorescent layer in green, the number of nonfluorescent layers in black/white, and the chemical structures of the fluorescently labeled poly(allylamine hydrochloride) (PAH) and the dyes shown in the bottom part. (Reproduced with permission from ref. 80. Copyright 2006, American Chemical Society.)

electron microscopy. De la Fuente and co-workers[82] reported the derivatization of tiopronin-protected AuNPs with ethylenediamine and bis(3-aminopropyl) terminated PEG and their functionalization with the GRGDSP peptide sequence. The particles were subsequently tested in vitro with a human fibroblast cell line to determine the biocompatibility and the cell-particle interactions, using fluorescence and scanning electron microscopies. The results indicated that the tiopronin–AuNPs derivatized with ethylenediamine induced endocytosis without any observed cell-death, while the tiopronin–AuNPs derivatized with the PEG derivative showed high affinity for cell surface receptor mainly due to ligand-receptor interactions. The internalization without toxicity offers the opportunity to introduce drugs or DNA into the cell cytoplasm using the AuNPs as vehicles, whereas the specific attachment to the cell surface allows the labeling of cell receptors with AuNPs and mapping of specific cell types. Liu *et al.*[83] have recently synthesized bioconjugates of mixed PEG/peptide monolayers on AuNPs through incubation of citrate-capped AuNPs with thiolated PEG and cysteine-terminated peptide, and characterized their stability in high ionic strength media. PEG length and particle size are two important adjustable parameters for creating stable peptide/AuNP conjugates capable of being internalized into cells. However, the functional immobilization of proteins on nanoparticles is often difficult to achieve because the occurrence of multiple functional groups in proteins complicates the task of linking them to nanoparticle surfaces while keeping them fully functional. Becker *et al.*[84] demonstrated that N-terminal modification of a small protein, GTPase Rab6A, with a thiolated PEG linker by native chemical ligation represented an efficient way of preparing proteins for immobilization on DNA-functionalized AuNPs. A place-exchange reaction with the modified protein was used to displace thiolated oligonucleotides from AuNPs in order to efficiently immobilize the protein on the AuNPs. The protein functionalized AuNPs have great potential for applications as probes in bioanalytical assays and as building blocks for the bottom-up assembly of functional hybrid nanoarchitectures.

AuNPs have immense potential for cancer diagnosis and therapy on account of their SPR enhanced light scattering and absorption.[85] They efficiently convert absorbed light into local heat. The near infrared region (650–900 nm) is ideally suited for *in vivo* imaging and photothermal therapy of cancer due to minimum absorption by intrinsic chromophores, hemoglobin (<650 nm) and water (>900 nm), this leading to a maximal penetration of radiation into tissues.[86] By changing the shape or composition of AuNPs, the SPR can be tuned to the near-infrared region. Gold nanorods, rod-shaped AuNPs, show transverse and longitudinal SPR bands in the visible (~520 nm) and the near-infrared regions, respectively. Niidome *et al.*[87] reported a modification of strongly cytotoxic gold nanorods by preparing them in hexadecyltrimethylammonium bromide (CTAB) solution using thiolated PEG. PEG-modified AuNPs showed a nearly neutral surface with little cytotoxicity *in vitro*, and should be suitable for medical applications.

For targeted drug delivery, a common approach is the active tissue targeting, where a ligand that recognizes a specific cell receptor is displayed on the delivery vehicle. The second approach, passive targeting, relies on the accumulation of drug carriers in target tissues due to nonspecific effects related to the physicochemical characteristics of the carrier. Thus, the development of targeted vehicles for efficient and effective drug delivery relies on optimizing both the cell-targeting ligand and the physicochemical characteristics of the carrier.[88] An important tool in the design of targeted delivery vehicles is a nanoparticle platform in which the physicochemical parameters can be independently controlled for *in vivo* evaluation. Bergen *et al.*[88] presented a versatile platform based on modified AuNPs in which nanoparticle formulations of varying particle size, surface charge, surface hydrophilicity, and galactose ligand density were prepared by conjugation of PEG-thiol and galactose-PEG-thiol to gold colloids. This platform was applied to screen for nanoparticle formulations that demonstrate hepatocyte-targeted delivery *in vivo*. Nanoparticle size and the presence of galactose ligands were found to significantly impact the targeting efficiency. Thus, this platform can be readily applied to determine design parameters for targeted drug delivery systems.

Of particular interest is the conjugation of AuNPs with smart polymers such as PNIPAM, because these hybrid systems have exhibited tailored electronic and optical properties through controlled interparticle separations in response to temperature stimulus. Zhao *et al.*[89,90] prepared a well-dispersed AuNP-PNIPAM hydrogel composite with thermo-switchable electrical properties by the copolymerization of NIPAM monomer and AuNPs pre-formed using a mixture of allyl mercaptan and *n*-dodecanethiol. It was found that the electrical properties of the composite may be tuned by temperature and the electrical conductivity changes by two orders of magnitude at the transition temperature of the composite. By changing the composition of the composite, such as the concentration of AuNPs and the cross-linking degree, the transition temperature can be changed from 0 to 40 °C. Seker *et al.*[91] demonstrated a method for making nanostructured composites featuring simultaneous switching of several optical properties such as color, transparency and metallic luster. The composite films were prepared from concentrated solutions of PNIPAM-coated AuNPs by solvent casting. The PNIPAM-coated AuNPs were prepared by an approach where two different sulfur-based chain-end functionalities, thiol or disulfide, of PNIPAM chains were attached to citrate ion stabilized AuNPs through exchange of weakly bound citrate ions with PNIPAM chains. It was found that well-dispersed AuNPs coated with thermo-responsive PNIPAM shells of controlled thickness and architecture could be used to generate controlled interparticle separations that governed the optical properties of the composites. Singh and Lyon[92] explored a synthetic route toward hollow PNIPAM nanogels with a "seed and feed" method. The seed and feed method involves the initial formation of hydrophobic polymer nuclei, which act as seeds for the precipitation of the growing polymer (feed) chains. Here, AuNPs were used as seeds that were first prepared by citrate reduction, followed by adsorption of NH_2-terminated PNIPAM on AuNPs. The in situ polymerization of NIPAM onto the seeds of AuNPs was then carried out above the phase transition temperature of PNIPAM, resulting in a cross-linked PNIPAM shell around the Au core nanoparticles Etching of the Au core from the PNIPAM-coated particles with KCN resulted in hollow hydrogel nanoparticles. The sub-50 nm dimensions make the nanogels ideal for drug and gene delivery, for cellular imaging, as nanoreactors, as protective shells for enzymes and as transfection vectors in gene therapy.

To assemble AuNP films with ordered structures, Genson *et al.*[93] and Zubarev *et al.*[94] prepared AuNPs functionalized with amphiphilic polybutadiene-poly(ethylene glycol) (PB-PEG) V-shaped arms by esterification of PB-PEG chains to mercaptophenol-stabilized AuNPs (Fig. 13). Approximately 65 V-shaped molecules were tethered to a pre-formed AuNP, resulting in a high grafting density of 0.2 nm^2 per V-shaped molecule. This value reaches the limits of the dense packing of phenylbenzoate groups in the upright orientation. These amphiphilic AuNPs formed stable Langmuir monolayers at the air/water and the air/solid interfaces. At these interfaces, the binary polymer arms vertically segregated into a dense polymer corona, which surrounded AuNPs, preventing their large-scale agglomeration and keeping individual nanoparticles well-separated from each other and forming flattened, pancake nanostructures. Ujihara *et al.*[95] proposed a new method to fabricate a self-assembled functional copolymer/nanoparticle hybrid film using a newly designed amphiphilic dendrimer of poly(amido amine) (PAMAM) with an azacrown core, hexylene spacers, and octyl terminals as template. The amphiphilic dendrimer was spread on AuNP suspension and the exposed azacrown core of the dendrimer was used as an effective binding site for AuNPs. The adsorbed AuNPs in the monolayer were arranged in a hexagonal lattice with 14 dendrimer molecules bound on each AuNP, the dendrimers were localized only on the upper-half surface of AuNPs at the

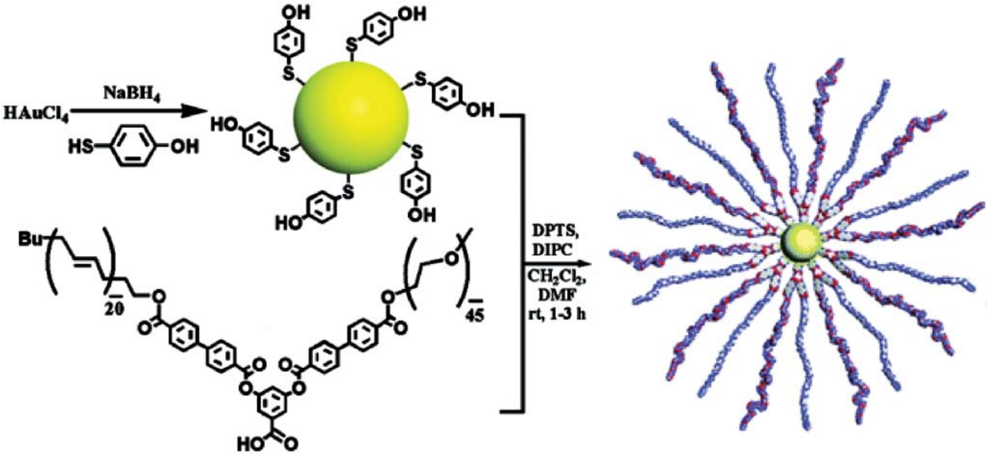

Fig. 13 Synthesis of amphiphilic Au(PB-PEG)$_n$ nanoparticles. (Adapted with permission from ref. 94. Copyright 2006, American Chemical Society.)

air/liquid interface (Fig. 14). Asymmetrically functionalizing NPs are of particular interest since they could directly lead to controlled patterning of NPs into complex structures for a variety of applications. Li and Li[96] demonstrated a novel approach to synthesize asymmetrically functionalized AuNPs using lamellar HS-PEO single crystals as the solid template to create a patterned functional (thiol) surface and to immobilize tetraoctylammonium bromide (TOAB)-protected AuNPs through Au–S bond (Fig. 15). The patterning of AuNPs on the surface of HS-PEO could be achieved, and the AuNP area density could be easily controlled by polymer molecular weight. Huang *et al.*[97] used a series of poly(oxypropylene)diamines of molecular weights from 230 to 4000 as ligands to induce citrate-capped AuNPs to self-assemble into well-ordered structures. The effect of the arrangement of ligand molecules with different chain lengths on the confined surfaces between two nanocrystals is most notable. Pan *et al.*[98] presented a dendrimer-mediated strategy for direct ordering of citrate-capped AuNPs into structured assemblies in water. The PAMAM dendrimers used were of generation 2–5 having surface thiol groups. One can directly control the interparticle distance through the choice of the dendrimer generation.

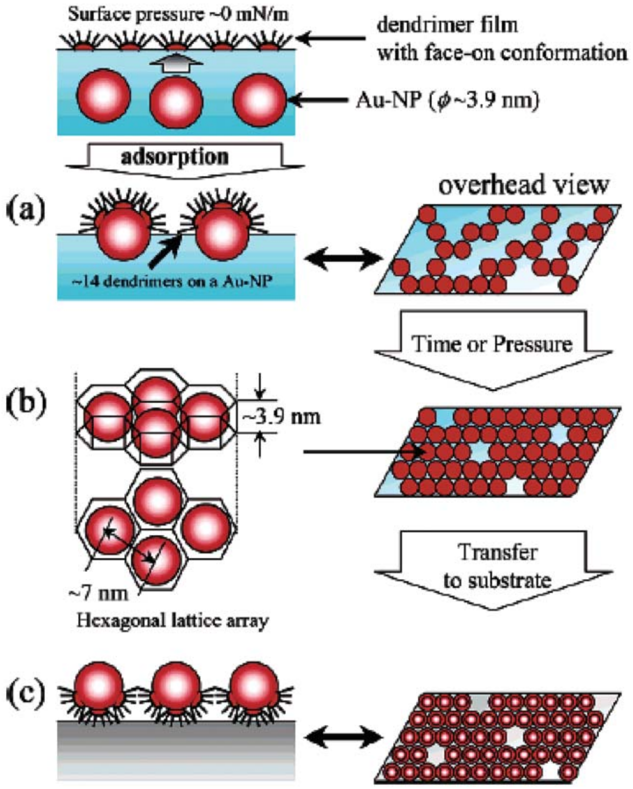

Fig. 14 Formation of the dendrimer/AuNP hybrid films *via* hybridization at the air/suspension interface and transfer onto a solid substrate. (Reproduced with permission from ref. 95. Copyright 2006, American Chemical Society.)

Composite materials with ordered structures consisting of conducting polymers and metal nanoparticles are of great interest and promising for further applications in micro- and optoelectronics. Intelmann *et al.*[99] prepared AuNPs on ultrathin films of polythiophene and polythiophene derivatives. The ultrathin films of polythiophene derivatives bearing hydroxyl groups were esterified with thioctic acid that contained a dithiolane moiety. The dithiolane moiety was utilised to immobilize AuNPs from a monodisperse gold sol synthesized by citrate reduction. The immobilized AuNPs were not removed by Scotch tape tests, indicative of the successful adhesion of AuNPs on the films of polythiophene derivatives through a covalent bond formed between the dithiolane moiety and gold. Cho and Park[100] reported the spontaneous deposition of Au and Ag NPs on sulfur containing conducting polymer surfaces of poly(3-methylthiophene) (P3MeT) and poly(3,4-ethylenedioxythiophene) (PEDOT) by simply dipping the polymer films into colloid solutions containing these particles. The current–voltage curves indicated that the contacts between the particles and the polymer surfaces were ohmic. This has been an important question for those wanting to use conducting polymers as substrates for electrocatalysts for fuel cells as well as for electronic devices, particularly for nanostructures.

A geometry that has drawn great interest recently is the metallic nanoshell, which consists of a dielectric spherical core, surrounded by a thin, uniform metallic shell. This

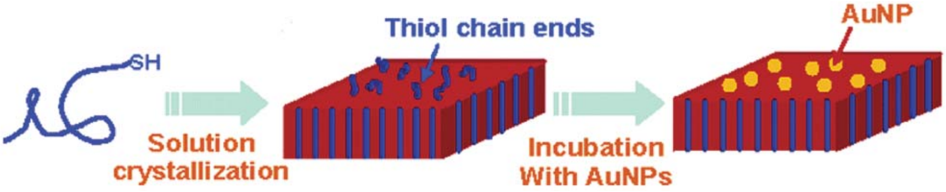

Fig. 15 Synthesis of asymmetrically functionalized AuNPs by immobilizing TOAB-protected AuNPs ($\sim$5 nm in diameter) onto the surface of square-shaped lamellar single crystals of HS-PEO. (Reproduced with permission from ref. 96. Copyright 2007, American Chemical Society.)

nanostructure has unique optical properties. By changing the relative sizes of the core and the shell, the SPR can be broadly tuned, as has been shown by Halas and co-workers who prepared gold nanoshells on silica particles.[101,102] Shi *et al.*[103] synthesized core–shell structures consisting of monodisperse PS latex nanospheres as cores and AuNPs as shells. AuNPs in a size range from 1 to 20 nm were first prepared by reduction of a gold precursor with sodium citrate or tetrakis(hydroxymethyl)phosphonium chloride. Carboxylate-modified PS spheres were functionalized into thiol-modified ones where thiols were located on the surface of the PS spheres. AuNPs were then bound to the thiol groups to provide up to about 50% coverage of the surface. These bound AuNPs served as seeds for the growth of a continuous gold shell by reduction of additional gold precursor. The shell thickness and roughness can be controlled by the size of the nanoparticle seeds as well as by the process of their growth into a continuous shell. By variation of the relative sizes of the latex core and the thickness of the gold layer, the SPR of the gold nanoshell can be tuned to specific wavelengths across the visible and infrared range of the electromagnetic spectrum, for applications ranging from the construction of photonic crystals to biophotonics.

Polymer-protected AuNPs were also prepared by encapsulating preformed colloidal AuNPs with water-soluble conductive poly(aniline-2-carboxylic acid) by Englebienne and Hoonacker[104] The composite nanoparticles displayed significant enhancements in photonic performance when compared to the individual components, which seemed to result from the electronic interplay between the two materials in the hybrid structure. The enhanced photonic reactivity of the composite structure offers new opportunities for biosensing applications. Abed *et al.*[105] demonstrated a reversible binding of octanethiol-capped AuNPs to a polymeric solid support by using boronic-derivatized resins and the specific reaction of diol molecules with boronic acid. Chen *et al.*[106] prepared aggregates of citrate–AuNPs with poly(L-lysine) functionalized with Raman dye that were used as an active substrate for increasing the signal of surface enhanced Raman scattering (SERS).

2.4 Physisorption

The fabrication of metal and semiconductor NPs using surfactant- or polymer surfactant-stabilized reverse micelles has extensively been investigated in the past three decades.[107] Low-molecular-weight surfactant-stabilized reverse micellar ("water-in-oil") systems have been used as "nanoreactors/templates" during the synthesis of AuNPs to obtain these materials with controlled sizes, a narrow size distribution and long-term stability.[108] This approach has also been referred to as "templating," since the characteristic features of the accordingly formed AuNPs are in principle fixed by the corresponding features of the "nanoreactors" formed by the self-assembling surfactants. Moreover, amphiphilic block copolymer micelles have been considered because they offer some advantages compared to the classical surfactants.[50,109] (1) The critical micelle concentration (cmc) of block copolymers is much smaller, and their kinetic stability is higher than that of low-MW surfactants. (2) The size and shape of block copolymer micelles can be easily tuned by varying the composition of the copolymer, the length of the constituent blocks, and the architecture of the copolymer. (3) The stability of the accordingly formed nanoparticles can be enhanced by increasing the length of the coronal blocks. In such reverse micellar systems, the hydrophobic block forms the corona, which provides stabilization, while the hydrophilic block forms the core, where metal precursors are able to dissolve due to coordination. The subsequent nucleation and growth of metal nanoparticles upon reduction are restricted to the meso/nanoscale level and the size and morphology of the resulting colloidal metal nanoparticles depend on the size and morphology of the template micelles.

Hydrophobic polymers such as PS, PMMA and poly(*tert*-butyl methacrylate) (PtBMA) are unable to coordinate with metal NPs (Au and Ag). However, PS-*b*-P4(2)VP block copolymer inverse micelles have been widely used as templates for the synthesis of AuNPs[110,111] Hou and co-workers[112] recently reported that the micellization of PS-*b*-P4VP in chloroform can be induced by the complexation between the P4VP blocks and $HAuCl_4$, this leading to polymeric micelles with PS being the shell and P4VP/$HAuCl_4$ complex being the core. Reduction of $HAuCl_4$ within the core using hydrazine hydrate led to formation of *ca.* 15 nm AuNPs in the core. However, continuous addition of methanol into the solution until the methanol–chloroform ratio was 9 : 1 caused the core–shell reversion. Vesicle-like structures were formed with PS being the wall and protonated P4VP/AuNPs being the shell. The AuNPs can be either stabilized within the P4VP shell for months by protonation or released from the shell by deprotonation of the P4VP blocks. Lu and Yi[113] prepared a monolayer of $HAuCl_4$-containing surface micelles by spin-coating solution micelles formed by the self-assembly of the $HAuCl_4$-modified PS-*b*-P2VP block copolymer in toluene. After the block copolymer template was removed with oxygen plasma, highly ordered and uniformly sized metallic AuNPs were generated without any post or prior reduction treatments, that were an excellent catalyst system for the controllable synthesis of silicon nanowires with a narrow diameter distribution. The process was fully compatible with existing semiconductor processing techniques and can be readily integrated into device fabrication. Weigl *et al.*[114] demonstrated an approach to the fabrication of diamond nanotips and silicon pillars by use of AuNPs as nanomasks. AuNP arrays were obtained by depositing $HAuCl_4$ loaded PS-*b*-P2VP spherical reverse micelles in toluene onto a diamond or silicon substrate surface (resulting in a monolayer of spherical micelles showing a high degree of hexagonal order) followed by a plasma induced removal of the polymer. By applying these particles as nanomasks for subsequent reactive ion etching, the hexagonal pattern was transferred into the substrate resulting in a corresponding array of diamond nanotips or silicon nanopillars, respectively.

Variation of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) (Pluronic) block copolymer molecular characteristics, concentration and temperature allows for unique tunability of block copolymer self-assembly in the presence of selective solvents such as water.[115] Sakai and Alexandridis[116–120] reported a single-step synthesis and stabilization of AuNPs in aqueous PEO-PPO-PEO block copolymer solutions at ambient temperature, where PEO-PPO-PEO block copolymers proved very efficient as both a reductant and a colloidal stabilizer. It has been suggested that PPO blocks can not directly contribute to the reduction of metal ions but can help enhance the reactivity of the PEO blocks with metal ions.[121] However, Sakai *et al.* found that both PEO and PPO blocks contributed to the $AuCl_4$-reduction but the PEO contribution appeared to be dominant. No major contribution of block copolymer micelles was observed to the AuNP size determination, but adsorption of hydrophobic PPO blocks on the surface of gold cores limited the particle growth and increased colloidal stability. However, the reaction activity due to PEO block length affects the particle growth more than the block copolymer adsorption. These authors also studied the effects of temperature on gold particle synthesis in aqueous solutions. Heating led to a particle size increase, suggesting that $AuCl_4^-$ reduction on the surface of gold particles was more significant than that in the bulk solutions. This can be understood in terms of heating-induced solution property changes (*e.g.*, increase in hydrophobicity and micelle concentration). Chen *et al.*[122] presented the effect of PEO-PPO-PEO block copolymer micelles and their hydrophobicity on the stabilization of AuNPs that were synthesized by the method developed by Sakai *et al.*[120] They observed that in time-dependent UV spectra an absorption at 300–400 nm provided evidence of primary gold clusters being formed at the very first step of the synthesis, and then, the gold clusters grew in size and were stabilized by block copolymer micelles. The stabilization capacities of the micelles were modulated by tuning the block copolymer concentration and composition and by adding salts. As the block copolymer concentration and/or molecular weight increased, its micelles were more efficient in stabilizing AuNPs. Efficient stabilization was necessary for obtaining AuNPs with uniform size and shape in a controlled manner. Otherwise aggregates and particles with irregular shapes such as triangular, hexagonal and rodlike were formed. Zheng *et al.*[123] used a thermo-responsive and pH-responsive triblock copolymer PEG-*b*-P4VP-*b*-PNIPAM as a template for synthesis of colloidal AuNPs with various morphologies. The template morphology of this triblock copolymer can be tuned from single chains, core–corona micelles to micellar clusters by simply changing pH or temperature of the aqueous solution. Discrete AuNPs, core–shell AuNPs and AuNP clusters were synthesized, respectively, corresponding to the template self-assembled by the triblock copolymer under certain conditions. Jewrajka and Chatterjee[124] synthesized amphiphilic AuNPs in aqueous solutions with di- and triblock copolymers of polymethacrylates. These block copolymers worked as both reducing and stabilizing agents. Polymer–AuNP nanocomposite films were prepared through the blending of appropriate amphiphilic AuNPs with the respective polymer matrices.

However, using block copolymer micelles as templates for the synthesis of AuNPs also brings several drawbacks. The long-term stability of micelles containing AuNPs is a critical factor that is very much dependent on the stability of block copolymer micelles, which can be affected by concentration of block copolymer, temperature, solvent and pressure.[125,126] For example, AuNPs started to aggregate to form large clusters with various shapes and sizes when the concentration of the block copolymer decreased and thus the copolymer chains were molecularly dispersed. On the other hand, the relatively large size of the templating core (generally of the order of 10 nm) impedes the formation of small AuNPs that are required for several applications; *e.g.*, only AuNPs smaller than 5 nm exhibit intense luminescence.[50,127] Unimolecular core–shell micelles from star-block copolymers[50,126,128] or shell cross-linked micelles[129] could circumvent these drawbacks for preparation of AuNPs. Compared to micelles formed by classical amphiphilic block copolymers, the unimolecular micelles offer a higher stability in solution since all the polymer chains are covalently bound to a core, no exchange between free chains and micelles is observed in the unimolecular micelles. Therefore, these objects are not characterized by a critical micellar concentration. Filali *et al.*[50] prepared AuNPs of improved stability against aggregation in the presence of five-armed star-block copolymers of PEO-*b*-PCL in organic solvents. A series of PEO-*b*-PCL star-block copolymers with a constant PEO core linked to PCL blocks of variable length were utilized. The PEO core was swollen with $KAuCl_4$ in DMF and AuNPs were subsequently obtained by reduction with $NaBH_4$. The average dimension (3–5 nm) of the formed AuNPs was in the same range for all star-block copolymers due to the same template PEO core. In sharp contrast, the size distribution and long-term stability against AuNP aggregation dispersed in DMF were strongly dependent on the PCL block length, confirming the role of PCL blocks as steric stabilizing blocks for these nanoparticles. In this respect, the long-term stability of the AuNPs decreases with decreasing the length of the PCL blocks. Li *et al.*[128] recently used reverse micelles of four-armed star-block copolymer, $(PS\text{-}b\text{-}P4VP)_4$, as nanoreactors for preparation of AuNPs. Zhang *et al.*[130] synthesized environmentally responsive PDMA brushes on the surface of polystyrene latex by ATRP, and the polymer brushes showed their transition temperatures of 31 °C at $pH = 10$ and 33 °C at $pH = 8$, respectively. PDMA domains were then used as nanoreactors to generate AuNPs on the surface of the colloid particles. These AuNP composites displayed effective catalytic activity in the reduction of 4-nitrophenol by $NaBH_4$.

Dendrimers are a special class of organic molecules on nanometer scale, the surfaces of which can be modified in various ways, while their interior cavities can serve as nanoreactors/templates for nanoparticle growth. In particular, PAMAM dendrimers having functional groups on their surfaces such as amine, sugar, methyl ester, alkyl and quaternary ammonium groups, have been recently reported as very effective nanoparticle stabilizers to prepare AuNPs.[131,132] Kim *et al.*[132] prepared highly monodisperse, 1–2-nm diameter AuNPs in water using PAMAM dendrimers having both quaternary ammonium groups and primary amines on their periphery. In the synthesis, they chose "magic number" ratios of [$HAuCl_4$] : [dendrimer] because it has previously been shown that AuNPs containing 55 or 140 atoms form energetically favorable structures.[133] When magic numbers of metal atoms were not used, the formation of a significantly more polydisperse population of AuNPs was observed. Crespilho *et al.*[134] reported the fabrication of nanostructured films comprising AuNPs-containing amine-terminated PAMAM dendrimers (generation 4) and poly-(vinylsulfonic acid) (PVS), through LbL technique on indium tin oxide (ITO) substrates. The hybrid films exhibited an enhanced charge transfer and may incorporate mediating redox substances, that may be exploited in biosensors requiring redox mediators.

Water-soluble polymers are able to coordinate with metal particles. Therefore, metal NPs have been typically produced in aqueous solutions in the presence of water-soluble polymers, where metal ions are reduced either by an added reductant or by the water-soluble polymers themselves. The water-soluble polymers which have been used for synthesis of AuNPs include both neutral and charged polymers such as poly(*N*-vinyl pyrrolidone),[135–139] poly(vinyl pyridine),[140,141] PEG,[142] PEG-*b*-PDMA,[143] poly(vinyl alcohol) (PVA),[144,145] poly(vinyl methyl ether) (PVME),[146] and polyelectrolytes such as PAA,[147] chitosan,[148,149] poly(ethyleneimine) (PEI, linear and branched),[150,151] and poly(diallyl dimethylammonium) chloride (PDDA).[152] Some of them such as poly(*N*-vinyl pyrrolidone), PEG, chitosan and polyelectrolytes act not only as stabilizers but also as reducing agents, that is, without addition of any other reductants.

However, concerns and problems remain in the case where AuNPs are stabilized through physisorption. The polymer chains are often non-specifically adsorbed onto the surfaces of AuNPs, rather than attached through one end of each polymer as was the case described above. In other words, the polymers adopt conformations where the polymer chains are wrapped around each gold core by physisorption and AuNPs are sterically and/or electrostatically stabilized against aggregation. Compared to covalent binding by which AuNPs are stabilized as described in subsections 2.1 and 2.2, AuNPs protected by physisorption show less long-term stability than the ones protected through covalent binding. As a result, a high concentration of protective agent is needed to attain colloidal stability of the nanoparticles.[153] Because of the less effective protection by physisorption, various shapes of Au particles such as spherical, polyhedral, rod-like, triangular and hexagonal plate-like structures with large sizes and broad size distribution have been produced.

One of the most frequently used polymeric protective agents in metal NPs synthesis is water-soluble poly(*N*-vinyl pyrrolidone). Zhou *et al.*[154] demonstrated a one-step thermal process to synthesize icosahedral AuNPs with a good uniformity by regulating the concentrations of poly(*N*-vinyl pyrrolidone) and $HAuCl_4$ or changing the temperature. However, some triangular and hexagonal structures were also found. Kan and co-workers[155] prepared Au microplates in high quantities and with regular shapes *via* thermal reduction (80–150 °C) of $HAuCl_4$ in ethylene glycol in the presence of poly(*N*-vinyl pyrrolidone). Thermal stability studies on the sample indicated that Au microplates were disintegrated into pieces when temperature exceeded 450 °C and that the melting and collapsing started mainly at the edges that should be Au (110) facets. Ah and co-workers[156] synthesized monodisperse size-controlled Au nanoplates with high purity by the reduction of $HAuCl_4$ with a reduced amount of sodium citrate in the presence of poly(*N*-vinyl pyrrolidone). These Au nanoplates can be used as single-crystalline substrates for the fabrication of arbitrary-shaped nanocomponents by postmachining. For example, a nanoletter and a nanogear were fabricated by focused ion beam (FIB) machining of the Au nanoplates (Fig. 16). Hoppe *et al.*[157] synthesized Au and Ag hydrosols in a one-step process by reduction of aqueous solutions of metal salts using poly(*N*-vinyl pyrrolidone) acting both as a stabilizer and a reducing agent. The polymer/metal molar ratio not only has an important effect on the size but also affects the shape of the obtained particles. The gradual decrease of the polymer/metal molar ratio led to a sharp increase in the size and polydispersity of the particles, as well as to the formation of increasing amounts of polyhedral, hexagonal and triangular plate-like structures. It was proposed that poly(*N*-vinyl pyrrolidone) acts as a reducing agent suffering a partial degradation during the nanoparticle synthesis. Two possible mechanisms were proposed to explain the reduction step: direct hydrogen abstraction induced by the metal ion and/or reducing action of macroradicals formed during the degradation of the polymer.

Diblock copolymers comprising a highly biocompatible poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC) block and a PDMA block can be used for the synthesis of sterically stabilized AuNPs in aqueous solution as reported by

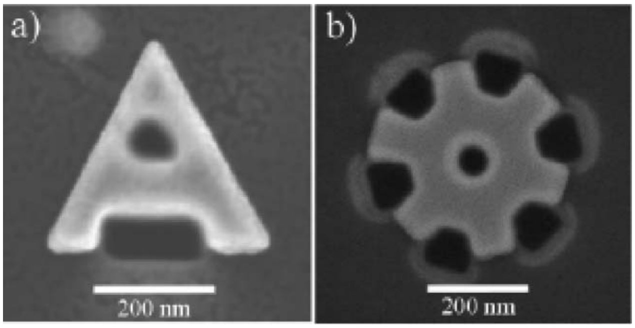

Fig. 16 (a) Nanoletter and (b) nanogear fabricated of gold nanoplates. (Reproduced with permission from ref. 156. Copyright 2005, American Chemical Society.)

Yuan and co-workers.[158] The PDMA block promotes the in-situ reduction of $AuCl_4^-$ to Au(0) and subsequently binds onto the surface of AuNPs, while the PMPC acts as a stabilizing block. These surface-functionalized biocompatible AuNPs would allow cell imaging and other biomedical applications.

PVME, a well-known thermo-responsive polymer, is soluble in water below its LCST at about 34 °C but phase separates due to the hydrophobic interactions of pendent methyl groups above that temperature. Bhattacharjee *et al.*[146] prepared thermo-responsive AuNPs by the borohydride reduction of a gold salt in the presence of PVME. The PVME-coated AuNPs assembled into large aggregates in the presence of polyelectrolytes at low pH upon an increase of solution temperature. This assembling process is reversible with respect to temperature and pH of the medium. TGA analysis indicated that AuNPs promoted the decomposition of PVME.

Using natural polymers as capping and/or reducing agents provides an approach for "green" nanoparticle preparation.[159,160] Chitosan, with excellent biodegradable and biocompatible characteristics, is a naturally occurring polysaccharide. Due to the unique polymeric cationic character of chitosan and its gel- and film-forming properties, chitosan has been extensively examined in the pharmaceutical industry for its potential use in the development of controlled release drug delivery systems. Using chitosan for the reduction and stabilization of AuNPs will not introduce any environmental toxicity or biological hazards. Huang and Yang[148] prepared AuNPs by reducing a gold salt with chitosan in the absence/presence of tripolyphosphate (TPP). The mechanism of the reduction where chitosan plays a role as a reducing agent is not clear. However, chitosan can be hydrolyzed in an aqueous acid to give D-glucosamine, a derivative of glucose that has been used as a reducing agent in the preparation of metal NPs.[160] On the other hand, the CH_2-OH groups in chitosan may also act as reductants in the formation of AuNPs. More interestingly, the gelation of chitosan upon contacting with TPP polyanion can also affect the shape and size distribution of AuNPs. Polygonal AuNPs, as well as triangular and rectangular plate-like AuNPs were obtained in addition to spherical AuNPs. Wang *et al.*[149] demonstrated a method for the synthesis of AuNPs on poly(dimethylsiloxane) (PDMS) surfaces by the incubation of chitosan-patterned PDMS films in a $HAuCl_4$ solution. The proposed mechanism was that chitosan molecules adsorbed on the PDMS surfaces acted as reducing/stabilizing agents, and the AuNP synthesis was localized within the regions capped with chitosan only. Surface-induced fluorescence quenching was observed in the regions capped with AuNPs, as well. Spider silk is an interesting natural polymer composed of fibroin proteins (MW 200000–300000) with excellent resilience and mechanical properties. Singh *et al.*[161] illustrated the use of spider silk as an active template for the spontaneous reduction of gold ions and the consequent one-step formation of AuNPs-loaded spider silk nanobioconjugates. The product is a promising candidate for the development of materials for vapor-sensing applications. Arabic gum (AG) is a widely accepted ingredient within food and pharmaceutical industry. It is a highly branched polysaccharide consisting of a complex mixture of potassium, calcium and magnesium salts derived from arabic acid, with galactose, rhamose, glucuronic acid, 4-*O*-methyl glucuronic acid and arabinose residues. For potential applications in nanomedicine, Kattumuri *et al.*[162] developed a new class of hybrid AuNPs within the AG matrix that provided *in vitro* and *in vivo* stabilities and realistic implications for the safe delivery of nanoparticles for a variety of diagnostic and therapeutic applications.

Mallick *et al.*[163] described a facile synthesis route for the preparation of a poly-(*o*-aminophenol)–AuNP composite material in methanol by polymerization of *o*-aminophenol (AP) monomer using $HAuCl_4$ as the oxidant. The formation of AuNPs and polymerization of AP took place simultaneously, and the resulting AuNPs were uniformly dispersed and highly stabilized throughout the polymer matrix that formed a uniform metal–polymer composite material without phase separation. Because polyAP is one of the polyaniline derivatives, the prepared polyAP–AuNP composite material as an electrically conducting polymer will have potential applications in optical and micro-electronic devices.

Ionic liquids (ILs), which are regarded as environmentally benign solvents because of their nonvolatility and high stability, have also been applied in the preparation of AuNPs. Kim *et al.*[164] reported a one-phase synthesis of Au and Pt NPs using new thiol-functionalized ionic liquids as stabilizing agents. Itoh *et al.*[165] demonstrated the synthesis of AuNPs using a disulfide-containing imidazolium ionic liquid as a stabilizer. Tatumi and Fujihara[166] prepared a series of novel AuNPs stabilized by a zwitterionic imidazolium sulfonate-terminated thiol. These zwitter–AuNPs showed great stability in water with high concentrations of electrolytes, ionic liquids and proteins. Zhao *et al.*[167] used an IL homopolymer, poly(1-methyl-3-(4-vinylbenzyl)imidazolium chloride), composed entirely of imidazolium units incorporating a hydrophobic benzyl group, as stabilizers in Au, Pt and Pd NP synthesis. The synergism of the steric, electrostatic and micelle effects of the high-molecular-weight ionic liquid polymer was believed to facilitate the stabilization of the NPs. The NPs can be easily transferred from water to hydrophobic ILs without degradation or aggregation by anion exchange.

3 Conclusion and prospects

The successful synthesis of AuNPs protected with polymers *via* various approaches has enabled us to obtain core–shell structures of a new type of materials that are very stable either in the solid state or as colloids. The substances combine the properties of the metal nanoparticles and organic macromolecules. Successful particle synthesis has inspired the construction of well-defined and functionalized architectures such as 1D nanowires, 2D films and 3D nanodevices using the core–shell nanoparticles as building blocks for different applications.

The synthesis of monodisperse AuNPs is still challenging. Due to the simplicity of the "grafting to" technique, the excellent stability of the resultant AuNPs, and the high surface density of the polymer brush on gold nano-cores, future attempts will be directed toward the synthesis of monodisperse

AuNPs with polymer protection. Compared to the surface density values of polymer brushes on planar surfaces by surface-initiated polymerization,[15] it has been shown that much higher surface density values of polymer brushes on gold nano-cores may be obtained by the "grafting to" technique. Future efforts are required to investigate the conformations and interactions of the brush chains for better understanding of the structures and properties of the polymer brushes.

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