Amphiphilic multiblock copolymer stabilized Au nanoparticles

Binyang Du*, Bin Zhao, Pengjun Tao, Kezheng Yin, Ping Lei, Qi Wang

Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China

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Abstract

Stable gold nanoparticles (AuNPs) are synthesized in N,N-dimethylformamide (DMF) by using amphiphilic multiblock copolymer (P4VP–PS–P4VP)n containing multiple trithiocarbonate moieties or amphiphilic triblock copolymer (HS–P4VP–PS–P4VP–SH) with thiol end groups as protecting agents. Only isolated gold nanoparticles are obtained, which indicate that the multiple functional groups of a single polymer chain are grafted at the same time to the same nanoparticle. The sizes of the AuNPs are slightly increased with raising the concentration of gold salt for a given concentration of the copolymers, leading to the red shift of the surface plasmon resonance of the AuNPs. Fourier transform infrared (FTIR) spectra and scanning force microscopy (SFM) images confirm that the AuNPs are indeed wrapped by the block copolymers. With the amphiphilic characteristic of the block copolymers, the AuNPs can be successfully transferred from DMF into aqueous solution. An unexpected red shift of the surface plasmon resonance (SPR) of the AuNPs after solvent transfer is observed, which is mainly attributed to the dense protecting polymer layers on the surfaces of the AuNPs in aqueous solutions. Both the size and structure of nanoparticles are maintained after solvent transfer. The AuNPs in aqueous solutions can be stable for a wide range of pH value up to pH $\approx 9$. At strong basic condition with pH > 10, the AuNPs will aggregate. The effect of pH value on the stability of the AuNPs is reversible. The optical property of the AuNPs also slightly depends on the pH value.

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Keywords: Gold; Nanoparticles; Amphiphilic block copolymer; Solvent transfer

1. Introduction

Gold nanoparticles (AuNPs) have widely potential applications due to their unique physical properties, in particular their optical properties [1,2]. AuNPs often exhibit an absorption band in the visible spectrum, which is usually termed as surface plasmon resonance (SPR) [3]. The peak position of SPR can be manipulated by varying the size, shape, surface properties as well as the surrounding medium of the nanoparticles, which are the fundament for their applications in sensing, electronic or optic devices. Extensive research efforts thus have been paid to tune the size, shape and surface chemistry of AuNPs in a variety of solvents by using different methods [4–6].

Polymers, especially amphiphilic block copolymers, have been widely used as size-tuners, reducing, stabilizing or grafting agents for AuNPs [7–19]. For instance, thermoresponsive poly(N-isopropylacrylamide) (PNIPA) was used to prepare gold nanoparticles which can respond to the external thermal stimulus. It was found that the SPR of aqueous AuNPs–PNIPA solution can be tuned by controlling the temperature of the solutions [13,14]. Li et al. reported a fabrication of pH-responsive gold nanoparticles capped with poly(4-vinylpyridine) through surface-initiated atom-transfer radical polymerization and discussed the potential application of such nanocomposites as supporters and carriers in catalytic chemistry [20]. By employing the similar method, core–shell Au/copolymer hybrids with a core of gold nanoparticle and a shell of crosslinked PNIPA networks were designed in the same group, which clearly demonstrate thermosensitive characteristics and can be used to encapsulate small molecules or other nanoparticles by virtue of the shell-network scaffold [21]. Hydrophilic thermosensitive Pluronic triblock copolymers (poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (PEO–PPO–PEO)) were also used as a reducing agent and size-controller for the synthesis of gold nanoparticles in aqueous solution at different temperature [15–17]. Bae et al. [18] have even functionalized the PEO blocks in Pluronic copolymer with –SH groups and prepared shell cross-linked Pluronic micelles with gold nanoparticles.
which show a temperature dependence of optical property. Amphiphilic diblock copolymers containing PNIPA block were also applied to prepare amphiphilic thermosensitive AuNPs. Monolayer of these amphiphilic AuNPs were then prepared by using Langmuir–Blodgett method, which shows tunable optical property by controlling the distance or space among neighbor gold nanoparticles [19].

Usually, reversible addition–fragmentation transfer polymerization (RAFT) is used to obtain such polymers mentioned above for grafting to the AuNPs. These polymers have narrow distribution of molecular weight and contain functional groups such as thiol and dithioester. Multiblock copolymers containing trithiocarbonate moieties can also be obtained by using RAFT polymerization [22–25]. The trithiocarbonate moiety can then be cleaved by an amine, producing a polymer with thiol groups at both ends [26]. These provide facile approaches to obtain various polymers or block copolymers with multiple functional groups, which can interact with the gold nanoparticles. In the present work, an amphiphilic multiblock copolymer (P4VP–PS–P4VP) n containing trithiocarbonate moieties was first synthesized by a two steps copolymerization of monomer styrene (S) and 4-vinylpyridine (4VP) with application of cyclic trithiocarbonate (CTTC) as RAFT agent. The amphiphilic triblock copolymer with multiple thiol end groups, i.e. HS–P4VP–PS–P4VP–SH, was then obtained after amine treatment. With trithiocarbonate and thiol functional groups, the multiblock and triblock copolymers can be used as protecting agents for the preparation of gold nanoparticles. It is also possible to obtain 2D or 3D self-assemble structures of gold nanoparticles if the multiple functional groups cooperatively interact with many gold nanoparticles. The amphiphilic characteristic of the block copolymers may be utilized for the solvent transfer of nanoparticles from organic solvent into aqueous medium. With the P4VP blocks, the obtained nanoparticle may be responsive to the pH value of the environments. Here, the AuNPs samples were first prepared in DMF by using these amphiphilic block copolymers as protecting agents. The obtained AuNPs solutions were transferred to clean glass bottles and kept at room temperature for testing their stabilities. All of the AuNPs samples are stable for more than half year. The polymers used here have multiple trithiocarbonate or thiol groups, which can form covalent bond with AuNPs (S–Au bond) and then stabilize the AuNPs [7–19,27,28]. On the other hand, the pyridine groups in the polymer chains may also stabilize the AuNPs via the coordination of N atom [29]. Therefore, the AuNPs protected by these block copolymers are very stable in DMF solution and can be stored for long-term purposes.

By utilizing the amphiphilic characteristic of these copolymers, the AuNPs can be transferred from DMF into acidic water. The solvent transfers of nanoparticles from aqueous into organic media or from organic solvent into aqueous solution have been the subjects for intensive researches. Among these, the solvent transfer of metal nanoparticles from organic solvent into aqueous media is more important since many potential applications of the nanoparticles may require an aqueous environment. Amphiphilic small molecules have been mostly used to achieve these purposes [30–36]. Some studies have involved the use of homopolymer [36] or comb polymer [37], which can dissolve in both organic solvent and water. Fustin et al. recently reported a successful transfer of AuNPs from DMF phase into basic water phase by using a hydrophilic polymer (polyacrylic acid, PAA) with trithiocarbonate functional group [38]. In current experiments, the AuNPs can be also successfully transferred from organic phase into aqueous medium by functionalizing the AuNPs with amphiphilic block copolymers with multiple functional groups. The AuNPs in acidic water are stable for several months and responsive to the pH value of the aqueous solutions. UV–vis spectrum, Fourier transform infrared (FTIR) spectrum, transmission electron microscopy (TEM) and scanning force microscopy (SFM) were then used to characterize the optical property, morphology and structure of the stable AuNPs in DMF and in aqueous solution after solvent transfer, respectively.

2. Materials and methods

2.1. Chemicals

Some important chemicals used in current experiments are summarized as follows: hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O, Acros) and sodium borohydride (NaBH₄, 99%, Aldrich) were used as received. Styrene (Aldrich) and 4-vinylpyridine (Aldrich) were stirred over CaH₂ overnight and distilled under reduced pressure prior to use. N,N-Dimethylformamide (DMF, analytical grade) was purchased from Sinopharm Chemical Reagent Co. Ltd. (SCRC, China). For preparation of Au nanoparticles, the DMF was used as received. While for synthesis of multiblock copolymer, i.e. (poly(4-vinylpyridine)-b-polystyrene-b-poly(4-vinylpyridine))ₙ ((P4VP–PS–P4VP)ₙ), DMF was dried over 4 Å molecular sieve and distilled before use. All other chemicals were purchased from commercial sources and used without further purification.

2.2. Synthesis of (P4VP–PS–P4VP)ₙ multiblock copolymer by RAFT polymerization

The (P4VP–PS–P4VP)ₙ multiblock copolymer containing trithiocarbonate moieties (–S–CS–S–) was synthesized by RAFT polymerization in the presence of cyclic trithiocarbonate. The detailed synthetic methods and the characterization of the copolymers have been previously reported [39]. In the present work, three (P4VP–PS–P4VP)ₙ multiblock copolymers with various 4VP mole fraction and molecular weight were used. To obtain triblock copolymer with thiol end groups (HS–P4VP–PS–P4VP–SH), the trithiocarbonate moieties contained in the original multiblock copolymer were treated and cleaved by n-butylamine as follows: 40 mg of the original multiblock polymer was dissolved in 10 mL DMF in a round-bottom flask; 0.8 mL of n-butylamine was then added and stirred at room temperature for 96 h; The DMF solvent together with the remaining n-butylamine were evaporated under reduced pressure and 10 mL of DMF was again added into the flask to re-dissolve the product. Scheme 1 briefly schematizes the synthetic route and the structures of the multiblock copolymer and the triblock
copolymer after amine treatment. The number average molecular weight ($M_{n,o}$) and polydispersity index (PDIo, $M_{w,o}/M_{n,o}$) of the original multiblock copolymers and the corresponding triblock copolymers after amine treatment were shown in Table 1.

### 2.3. Preparation of gold nanoparticles

Au nanoparticles (AuNPs) were directly synthesized in a homogenous DMF solution with the presence of the multiblock copolymer or the triblock copolymer. Briefly, ~0.566 g DMF solution of the copolymer (4 mg/mL, 0.1 mM) was first added into a 25 mL round-bottom flask containing 10 mL DMF solvent under stirring. Preset amount of HAuCl₄ DMF solution (~0.478 g, ~2.39 g, and ~4.78 g, 8 mM) was then added and stirred for 5 min. Afterward, NaBH₄ DMF solution (16 mM, final molar ratio of NaBH₄/HAuCl₄ = 2.5:1) was added dropwise into the mixed solution under vigorously stirring for 5 min. The mixed solution was continuously vigorously stirred for 24 h. The samples were then left at least for 3 days at room temperature in order to decompose the residual NaBH₄ before any further experiments. The DMF solutions of HAuCl₄ and NaBH₄ were newly prepared before use since they are unstable in air at room temperature. The attempts to purify the gold nanoparticles by centrifugation at 16,000 rpm with 5 mL tube for 20 min were failed. Only large particles can be precipitated. The possible reason is that most of the nanoparticles are too small to be completely precipitated with current centrifuge.

It is known that P4VP–PS type block copolymers form stable micelles in aqueous solution with pH < 5 [40]. The hydrophobic PS block forms the core of the micelle, while the hydrophilic P4VP block is the outer shell of the micelle since the P4VP block is soluble in water with pH < 5 [40]. Hence, the AuNPs synthesized in DMF may be transferred into aqueous solution. In order to achieve this purpose, the samples mentioned above were first added with about 10% acidic water (pH ≈ 3) and then dialyzed (MW cut-off 3500) in large amount of acidic water with pH ≈ 3 for at least 7 days. The acidic water was regularly refreshed in order to completely get rid of the DMF solvent. Table 2 summarizes the preparation parameters and some related properties of the AuNPs samples prepared in the present experiments.

Depending the copolymer, the amount of HAuCl₄ and the final solvent used, the samples were coded as: (protecting copolymer)–(amount of HAuCl₄)–solvent. For example, MP1–Au1–DMF means that the protecting copolymer is the original multiblock copolymer MP1 with multiple trithiocarbonate moieties, the initial concentration of HAuCl₄ is ~0.478 g, and the solvent is DMF. Note we here set ~0.478 g HAuCl₄ as code Au1. While TP3–Au10–H₂O means

### Table 1

<table>
<thead>
<tr>
<th>Multiblock polymer</th>
<th>4VP% (mol%)</th>
<th>$M_{n,o}$ ($10^4$)</th>
<th>PDIo</th>
<th>Corresponding triblock polymer</th>
<th>$M_{n,o}$ ($10^4$)</th>
<th>PDIo</th>
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<tr>
<td>MP1</td>
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<td>2.19</td>
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<td>2.49</td>
<td>1.13</td>
</tr>
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<td>61.2</td>
<td>11.0</td>
<td>1.89</td>
<td>TP2</td>
<td>2.88</td>
<td>1.19</td>
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<td>1.74</td>
<td>TP3</td>
<td>3.75</td>
<td>1.15</td>
</tr>
</tbody>
</table>
that the protecting copolymer is the triblock copolymer TP3 with thiol end groups, the initial concentration of HAuCl₄ is that the protecting copolymer is the triblock copolymer TP3 with thiol end groups, the initial concentration of HAuCl₄ is ~4.78 g, and the solvent is H₂O after solvent transfer.

### 2.4. Characterization of gold nanoparticles

The optical absorptions of the gold nanoparticle solutions were recorded by using a Cary 100 Bio UV–vis spectrophotometer. Fourier transform infrared and Raman spectra were used to check whether the copolymers grafted to the gold nanoparticles. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. Raman spectra were obtained on an Almega dispersive Raman microscope (Thermo Nicolet) with an argon laser 532 nm. The size and morphology of the gold nanoparticles were investigated by using transmission electron microscopy and scanning force microscopy, respectively. The TEM measurements were performed on a JEOL JEM-1200 electron microscope operating at an acceleration voltage of 60 kV. TEM samples were prepared by dip-coating with carbon-coated copper grids into the DMF solutions of Au nanoparticles or Formvar-coated copper grids into the aqueous solutions of Au nanoparticles. The solvent was gently absorbed away by a filter paper. The grids were then allowed to dry in air at room temperature before observation. Note that the TEM samples were not stained by any chemical species. The particle sizes (diameter) of the AuNPs from the TEM pictures were calculated by using ImageJ. If the contrast of the TEM pictures was too low to use ImageJ, several tens of particles were then directly measured and the mean size was calculated. The SFM measurements were performed on a Seiko SPM3800N station in the tapping mode. The resonance frequency of the Si-cantilever (NSG10, NT-MDT) was about 300 kHz. SFM Samples were prepared by casting a droplet of the Au nanoparticle solutions onto the freshly cleaved mica and then dried in vacuum at room temperature.

### 3. Results and discussion

#### 3.1. Effects of capping polymer used

Isolated noble metal nanoparticles show a strong absorption band in the visible light region, i.e. the so-called surface plasmon resonance [41]. Fig. 1 shows the UV/vis spectra of the AuNP samples in DMF solution with different capping copolymers. All the UV/vis curves show a maximum absorption at around 516–530 nm, which is typical for the gold nanoparticles. Clearly, the structure sequence and molecular weights of the capping copolymers do not have systematical effects on the optical properties of the AuNPs.

The morphology, size and structure of the AuNPs were investigated by TEM and SFM. Fig. 2 shows the typical TEM pictures of the AuNPs prepared in DMF solutions. The gold nanoparticles capped with amphiphilic block copolymers in DMF are spherical in shape and show a relative narrow size distribution. Since the purification of the AuNPs was unsuccessful, gray patches of the excess polymers can be observed in some regions (cf. Fig. 2b). The peak positions (the absorbance maximum wavelength, λₘₐₓ) of SPRs and the mean sizes of the AuNPs samples are collected in Table 2.

![Fig. 1. The optical absorption spectra of the AuNPs samples directly prepared in DMF (a) using various multiblock copolymers as protecting agent and (b) using the corresponding triblock copolymers as protecting agent.](image)

<table>
<thead>
<tr>
<th>Code</th>
<th>λₘₐₓ of SPR (nm)</th>
<th>Mean particle size (nm)</th>
<th>Code</th>
<th>λₘₐₓ of SPR (nm)</th>
<th>Mean particle size (nm)</th>
</tr>
</thead>
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<tr>
<td>MP1–Au1–DMF</td>
<td>522</td>
<td>4.8(±3.7)</td>
<td>TP1–Au1–DMF</td>
<td>525</td>
<td>4.5(±3.3)</td>
</tr>
<tr>
<td>MP2–Au1–DMF</td>
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<td>519</td>
<td>4.5(±3.1)</td>
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<tr>
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<td>4.1(±2.7)</td>
<td>TP3–Au1–DMF</td>
<td>527</td>
<td>5.4(±4.0)</td>
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<tr>
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<td>TP3–Au5–DMF</td>
<td>529</td>
<td>3.7(±4.3)</td>
</tr>
<tr>
<td>MP3–Au10–DMF</td>
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<td>8.0(±6.5)</td>
<td>TP3–Au10–DMF</td>
<td>536</td>
<td>6.5(±4.0)</td>
</tr>
<tr>
<td>MP3–Au1–H₂O</td>
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<td>3.9(±2.3)</td>
<td>TP3–Au1–H₂O</td>
<td>534</td>
<td>5.2(±2.2)</td>
</tr>
<tr>
<td>MP3–Au5–H₂O</td>
<td>537</td>
<td>5.9(±5.4)</td>
<td>TP3–Au5–H₂O</td>
<td>536</td>
<td>5.9(±4.6)</td>
</tr>
<tr>
<td>MP3–Au10–H₂O</td>
<td>543</td>
<td>6.9(±5.1)</td>
<td>TP3–Au10–H₂O</td>
<td>542</td>
<td>6.5(±4.7)</td>
</tr>
</tbody>
</table>

* Calculated by measuring about 30–40 individual gold nanoparticles.
leading to the large phase-drag for polymer layers in response to the external tapping of the SFM tip. At certain condition, the SFM tip can even sense the gold core under the protecting polymer layers. Hence, the dark regions in the phase image can be attributed to the gold nanoparticles, while the white peripheral regions correspond to the capping polymer layers. FTIR spectra further confirm that the copolymers indeed grafted to the gold nanoparticles (see below).

Since there are two thiol end groups in a molecular chain of the triblock copolymer and more than two trithiocarbonate moieties in a molecular chain of the multiblock copolymer, it may be possible for a polymer chain to graft with two or more gold nanoparticles at the same time. Hence, network-like or bridge structures of the AuNPs may be expected. However, not such structures of AuNPs are observed for all of the AuNPs samples in DMF. Only isolated gold nanoparticles are observed (for
example see Fig. 2). Therefore, it might be concluded that a single molecular chain of the block copolymers is capped to the same gold nanoparticle. In another word, the multiple functional groups of the copolymer chain, i.e. thiol end groups or trithiocarbonate moieties, are grafted to the same gold nanoparticle. It may be attributed to the conformation flexibility of the polymer chains.

### 3.2. Effects of gold sol concentration

The effects of the gold sol concentration on the properties of the resulted AuNPs were checked. MP3 and TP3 were selected as protecting agents. During the preparation of AuNPs, the concentration of copolymers was fixed while the amount of gold sol was varied. Fig. 4 shows the UV/vis spectra of the AuNP samples in DMF solution with various concentration of gold sol. With increasing the concentration of HAuCl₄ in the reaction solution, the surface plasmon resonance of the AuNPs in DMF solutions is broadened and slightly shifted to the longer wavelength, i.e. red shift.

The peak position of the absorption band of noble nanoparticles, i.e. \( \lambda_{\text{max}} \), is known to depend on various parameters of the nanoparticle solutions, such as particle size, particle shape, surface-capping agents as well as the dielectric property of the surrounding medium [37,45]. A red shift of \( \lambda_{\text{max}} \) may be attributed to the large particle size or higher refractive index of the surrounding medium. Since the AuNPs are stable in DMF solutions for several months, it means that the amount of amphiphilic multiblock copolymers used is enough to protect all of the gold nanoparticles regardless of the initial HAuCl₄ concentration. On the other hand, if the copolymers were not enough for protecting the gold nanoparticles at higher HAuCl₄ concentration, a blue shift of SPR should be observed since the refractive indexes of polymers (for example the refractive index of PS, \( n = 1.59 \)) [46] are much larger than that of DMF (1.4282) [47]. Hence, the red shift of SPR with raising HAuCl₄ concentration may be attributed to the increase of particle size, which is verified by TEM.

Fig. 5 shows the typical TEM pictures of the AuNPs obtained with MP3 as protecting agent and different concentration of gold sol in DMF. The sizes and polydispersities of the AuNPs slightly increase with raising the initial HAuCl₄ concentration, which are consistent with the optical properties of the AuNPs in DMF, i.e. the red shift and broaden of the SPR with increasing the HAuCl₄ concentration. The peak positions (\( \lambda_{\text{max}} \)) of SPRs and the sizes of the AuNPs are also listed in Table 2.

The AuNPs samples obtained with highest gold sol concentration in the present work (i.e. MP3–Au10 and TP3–Au10) were centrifuged although only large particles can be precipitated. The precipitates were then collected for FTIR and Raman spectrum measurements. Fig. 6 shows the FTIR of the AuNPs and the corresponding pure multiblock copolymers. The FTIR spectra of the particles and of pure copolymers are similar, which further indicates that the gold nanoparticles are indeed protected by the copolymers. The thiol groups will exhibit a characteristic bands at around 2600–2550 cm⁻¹ (\( \nu(S-H) \)), while the trithiocarbonate groups will have characteristic bands at around 1250–1000 cm⁻¹ (\( \nu(C=S) \)) and 790–630 cm⁻¹ (\( \nu(C=S) \)). However, these groups can neither be detected by FTIR nor by the Raman spectra in the present experiments, which may be due to the small amount of function groups in the copolymers. Nevertheless, it can still be concluded that the gold nanoparticles are indeed protected by the copolymers.

### 3.3. Solvent transfer of the AuNPs from DMF into acidic water

The amphiphilic P4VP–PS type block copolymers can form stable micelles with hydrophobic cores of PS and hydrophilic shell of P4VP in aqueous solution with pH < 5 [40]. With this amphiphilic characteristic of the multiblock copolymers, the AuNPs were successfully transferred from DMF into acidic water (pH ~ 3). The AuNPs in acidic water can be stable for several months. Note that only AuNPs samples capped with MP3 and TP3 were transferred from DMF into acidic water. As discussed above, the size and polydispersity of the AuNPs in DMF slightly increase with raising the initial HAuCl₄ concentration (cf. Fig. 5). As a consequence, the SPR of the AuNPs in acidic water after solvent transfer shows the similar tendency. Fig. 7 shows the optical absorption spectra of the AuNPs samples in acidic water after solvent transfer. With raising HAuCl₄ concentration, the SPR of the AuNPs in acidic water shifts to the longer wavelength, i.e. red shift. It can be also seen that for a given AuNPs sample, the surface plasmon resonance is broad-
Fig. 5. Typical TEM pictures of the AuNPs directly prepared in DMF with protecting copolymer MP3 and different HAuCl₄ concentrations. (a) MP3–Au1–DMF; (b) MP3–Au5–DMF; (c) MP3–Au10–DMF; (d) the size distribution of (a); (e) the size distribution of (b); and (f) the size distribution of (c).

The morphology, size and structure of the AuNPs were also investigated by TEM and SFM. TEM results (Fig. 8) show that the AuNPs still keep the spherical shape in acidic water after solvent transfer, which is similar to those in DMF. The gray patches in Fig. 8a indicate that the excess amphiphilic block copolymers form spherical micelles in the acidic water as expected [40]. The SFM images are shown in Fig. 9 for the AuNPs after solvent transfer. The gold nanoparticles and polymer protecting layers result in a clear contrast of the phase image for the AuNPs, corresponding to the dark and white regions, respectively (Fig. 9b). The height of the gold nanoparticles is about 3–6 nm, which is consistent with those obtained in Fig. 3, i.e. AuNPs in DMF. The...
Fig. 6. FTIR spectra of the AuNPs samples, i.e. MP3–Au10–DMF and TP3–Au10–DMF, and the corresponding pure copolymers, i.e. MP3 and TP3.

lateral size of AuNPs is again much larger than those obtained by TEM and similar to those obtained in Fig. 3. These results indicate that the solvent transfer from DMF into acidic water does not strongly affect the morphology, size and structure of the AuNPs. The peak positions ($\lambda_{\text{max}}$) of SPRs and the mean size of the AuNPs samples in acidic water after solvent transfer were also shown in Table 2.

3.4. Optical property of the AuNPs in acidic water

Interestingly, an unexpected red shift of SPR is observed when the AuNPs were transferred from DMF into acidic water with pH $\sim 3$ (cf. Fig. 7). A blue shift of SPR may be expected when the AuNPs are transferred from a solvent with higher refractive index into a solvent with lower refractive index, i.e. from DMF into water (1.33) [45]. Instead, a red shift is observed here for AuNPs after solvent transfer from DMF into water although the refractive index of water is smaller than that of DMF.

A possible reason for this red shift of SPR after solvent transfer may be the surface charge of the AuNPs in aqueous solution. Peng et al. [35] observed a blue shift of SPR when AuNPs capped with 4-aminothiophenol (4-ATP) were transferred from water into toluene phase by tuning the pH value of the solution. A broadening of absorption band was also observed after solvent transfer. They attributed the blue shift of SPR to the difference in the surface charge of the nanoparticles in water and toluene phases. Previous studies have shown that the nanoparticles with negative or zero charge show a blue shift of SPR compared to those with positive charge, vice versa [48–50]. For AuNPs capped with 4-ATP, the amino moieties are protonated in water with pH $\sim 3.0$, resulting in a highly positive-charged particle surface, while in toluene the charge density on the particle surface is much lower. Similarly, the pyridine moieties of the P4VP–PS–P4VP multiblock copolymer will be protonated under acid condition. Thus, when the AuNPs capped with P4VP–PS–P4VP were transferred from DMF into acidic water with pH $\sim 3.0$, the surface charges of AuNPs are positive due to the protonation of pyridine groups. The surface charge density of AuNPs in acidic water is then much larger than that of AuNPs in DMF phase, which may result in the red shift of SPR for AuNPs in acidic water.

Another possible contribution to the red shift of SPR after solvent transfer is the dense packing of the polystyrene blocks onto the nanoparticle surfaces in acidic water since polystyrene is hydrophobic and unsolvable in water. The refractive index of polystyrene is about 1.59 and much higher than those of DMF and water. DMF is a good solvent for both P4VP and PS blocks. Hence, the molecular chains of the block copolymers will swell in DMF, leading to a loose packing on the nanoparticle surface. The AuNPs tend to be exposed to the dielectric DMF. While acidic water is a non-solvent for PS blocks, the PS blocks will then accumulate onto the surfaces of AuNPs and form a dense packing layer in water. Thus, the AuNPs are well surrounded by the polymer and less exposed to the water medium. It has been shown that for alkylthiol-protected gold nanoparticles, the
refractive index of the alkylthiol layer dominates the SPR of the AuNPs while the effect of the solvent refractive index is less important [37]. For AuNPs protected by P4VP–PS–P4VP in water, the effect of the polymer refractive index on the SPR of AuNPs may be important as well.

To test the above two possible contributions, certain amount of acidic water (pH \( \sim 3.0 \)) was added into the DMF solutions of AuNPs. It is found that with increasing the content of acidic water, the SPR of AuNPs in mix-solvent slightly shifted to blue, as shown in Fig. 10. With only 25\% acidic water, the peak position of SPR is even unaffected. While in pure acidic water after completely solvent transfer, a red shift of SPR is appeared. These phenomena suggest that the surface charges of the particles have less contribution to the SPR of AuNPs capped with the multiblock copolymers studied here. This conclusion is further confirmed by the optical properties of the AuNPs aqueous solutions with various pH values.

Fig. 11a shows the \( \lambda_{\text{max}} \) of SPR as a function of pH value for the AuNPs samples of TP3–Au10–H2O and MP3–Au10–H2O. The pH values of the AuNPs aqueous solutions were adjusted and calculated by using KOH and HCl aqueous solutions. The \( \lambda_{\text{max}} \) of SPR is almost constant in the range of pH \( \approx 2–9 \). When the pH value of the aqueous solution is increased from pH \( \approx 2 \) to \( \approx 9 \), the surface charges of gold nanoparticles is changed from positive charges to zero or negative charges due to the deprotonation of pyridine groups at higher pH value. However, the shapes of UV/vis spectra of AuNPs aqueous solution as well as the \( \lambda_{\text{max}} \) of SPR are nearly unchanged for pH values from
Fig. 9. SFM images of the AuNPs with amphiphilic triblock copolymer (HS–P4VP–PS–P4VP–SH) as stabilized agent in acidic water after solvent transfer, i.e. TP3–Au1–H2O. (a) Topography image and (b) phase image.

Fig. 10. The peak position of surface plasmon resonance (SPR) of the AuNPs samples (TP3–Au10 and MP3–Au10) as a function of the volume fraction of H2O, \( \phi_{H2O} \). The inset shows the optical absorption spectra of TP3–Au10 at different volume ratios of H2O/DMF.

pH \( \approx 2 \) to \( \approx 9 \) (Fig. 11b). These further confirm that the surface charges of the particles are less important for the optical properties of AuNPs capped with amphiphilic multiblock copolymers in aqueous solutions. The experimental results obtained here are contrast to those observed for gold nanoparticles purely capped with poly(4-vinylpyridine) (P4VP) homopolymer [20]. For Au/P4VP nanocomposite in aqueous solution, the SPR peak position was changed from 526 nm at pH 1.2 to 551 nm at pH 7.4, and a rapid jump from pH 2.0 to 4.0 with a critical point at pH 3.2 was also observed, which can be associated with the apparent dissociation constant (pK_a) of poly(4-vinylpyridine) [20]. In this case, the stability and surface chemistry of the Au/P4VP nanocomposite are mainly affected by the chemical properties of the P4VP chains. The surface charges of the gold nanoparticles have main contribution to the SPR. At a low pH (<3.2), the pyridyl rings are protonated and the Au/P4VP nanocomposites are stabilized by the electrostatic repulsive forces. While at higher pH (>3.2), the pyridine groups are uncharged and the coiling of the P4P chains will result in a mass particle aggregation, which lead to the red shift of SPR. In the current systems of Au nanoparticles capped with PS-P4VP block copolymer, the dense packing layers of PS dominate the refractive index of the AuNPs in aqueous solution, which mainly determine the optical properties of AuNPs in aqueous solution. The combination of the electrostatic repulsive interaction and the steric–solvation interaction of the protecting polymer layers may make the AuNPs

Fig. 11. (a) The peak position of surface plasmon resonance (SPR) of the AuNPs samples in aqueous solution (TP3–Au10–H2O and MP3–Au10–H2O) as a function of the pH value of the aqueous solution. (b) The selected optical absorption spectra of TP3–Au10–H2O at different pH values.
stable in aqueous solutions for a wide range of the pH value from pH ≈ 2 to ≈ 9 [40]. In the acidic condition, the pyridine groups are protonated to give positive charges around the gold nanoparticles. While in the basic condition, the P4VP block will release its α-H to give anionic block due to the amphiprotic properties of P4VP blocks in basic solvent [40]. In the neutral condition, the steric–solvation interaction of the protecting copolymer layers mainly contributes to the stability of the AuNPs.

However, the \( \lambda_{\text{max}} \) of SPR shifts to the red when the pH values of the aqueous solutions are larger than 10. At high pH value, the –SH groups may change into S\(^-\), which will damp the surface plasmon and lead to the red shift and broadening of SPR band [51]. However, precipitations of the AuNPs are found in 24 h after adjusting the pH value. Therefore, the increase of \( \lambda_{\text{max}} \) is mainly attributed to the aggregations of AuNPs at strong basic conditions. For the strong acidic conditions with pH < 2, a slightly blue shift of SPR is observed while the AuNPs are still stable.

The stability and optical properties of the AuNPs in aqueous solutions shows a reversible dependency on the pH value. The precipitations of the AuNPs in strong basic condition (pH > 10) are redispersed by adjusting the pH value back to acidic condition. The \( \lambda_{\text{max}} \) of SPR shifts back to the value of AuNPs aqueous solution with pH ≈ 2–9 as well. When the pH value of the solution is readjusted to pH > 10, the AuNPs aggregate and precipitate again.

Since the pH of the solution was adjusted by KOH and HCl solutions, the ionic strength of the AuNPs solution increased during the adjustment. For example, the ionic strength is about 0.1 M for pH ≈ 1. To further investigate the effect of ionic strength on the stability and optical properties of the AuNPs in acidic water after solvent transfer, the ionic strength of the AuNPs aqueous solution (pH ≈ 3) was adjusted by using 2.5 M KCl aqueous solution (pH ≈ 3) and the optical property of the AuNPs solution was monitored by UV–vis spectrum. It was found that the shape and the \( \lambda_{\text{max}} \) of SPR do not change for the AuNPs aqueous solution (pH ≈ 3) with salt concentration ranging from 0.05 M to 1.25 M. This indicates that the pH dependence of optical property of AuNPs aqueous solution is uncorrelated with the ionic strength of the solution. The AuNPs are stable in acidic water (pH ≈ 3) for the ionic strength ranging from 0.05 to 1.25.

4. Conclusion

Stable gold nanoparticles were directly synthesized in a homogeneous DMF phase by using amphiphilic multiblock copolymer containing multiple functional groups as stabilizing agents. The type of copolymers used only has small effects on the sizes and physical properties of the gold nanoparticles. The multiple functional groups of a single polymer chain are found to graft at the same time to the same gold nanoparticle since only uniformly dispersed and isolated AuNPs are observed. FTIR spectra and SFM measurements confirm that the copolymer indeed grafted to the AuNPs. The sizes of the AuNPs are slightly increased with raising the concentration of gold salt for a given concentration of the copolymers, leading to the red shift of the surface plasmon resonance of the AuNPs.

The AuNPs can be safely transferred from DMF into aqueous medium due to the amphiphilic characteristic of the multiblock copolymers. UV–vis spectrum shows a red shift of the SPR of the AuNPs after solvent transfer, which is mainly attributed to the dense packing of hydrophobic blocks onto the surfaces of the AuNPs in water. Both the size and structure of gold nanoparticles are still maintained after solvent transfer. The AuNPs in aqueous solutions are stable for a wide range of the pH value from pH ≈ 1 to ≈ 9 due to the electrostatic repulsive interaction and the steric–solvation interaction of the amphiphilic copolymers. The stability and optical property of the AuNPs in aqueous solutions also shows a reversible dependence on the pH value. The AuNPs are stable in acidic water (pH ≈ 3) after solvent transfer for the ionic strength ranging from 0.05 to 1.25.

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References
