



Size-controllable gold nanoparticles stabilized by PDEAEMA-based double hydrophilic graft copolymer

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ABSTRACT

Poly(*N*-isopropylacrylamide)-*b*-[poly(ethyl acrylate)-*g*-poly(2-(diethylamino)ethyl methacrylate)] (PNIPAM-*b*-(PEA-*g*-PDEAEMA)) double hydrophilic graft copolymers were employed to prepare stable colloidal gold nanoparticles *in situ* with controllable size in aqueous media without any external reducing agent. PDEAEMA side chains served as reduction agent and stabilizer and PNIPAM segment acted as a hydrated layer to enhance the stability of gold nanoparticles. These gold nanoparticles showed a remarkable colloidal stability without any observable flocculation or aggregation for at least 2 months and they were characterized by UV–vis, XRD, TEM and AFM in detail. The size of gold nanoparticles can be tuned by adjusting the length of PDEAEMA side chains and the molar ratio of [DEAEMA]/[AuCl₄⁻]. Both the increasing of the length of PDEAEMA side chains and the decreasing of [DEAEMA]/[AuCl₄⁻] molar ratio resulted in the fall of size.

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1. Introduction

Double hydrophilic copolymer represents a new class of amphiphilic copolymer, which consists of two different hydrophilic segments. This kind of copolymer can self-assemble into one or more types of micelles in water if one hydrophilic segment becomes hydrophobic accompanied by physical or chemical transformations such as temperature, pH, and ionic strength [1,2]. On the other hand, past investigations have revealed that double hydrophilic copolymer, with one hydrophilic segment interacting strongly with appropriate inorganic materials and another hydrophilic segment mainly promoting the solubilization in aqueous media, can exert a strong influence on the crystallization of inorganic crystals such as CaSO₄, BaSO₄, CdS and Au [3–6].

Gold nanoparticles have been extensively studied due to their special size effects including high third-order nonlinear susceptibility, large near-resonance nonlinear response, broad surface plasmon band in the region around 520 nm, high specific surface

area and unique catalytic activity [7]. These fascinating characteristics have been materialized to extend their applications in many fields such as catalysts, sensors and optoelectronics [7–11]. Growing interest in gold nanoparticles provides a progressive impetus to the development of their preparation methods including chemical reduction, photolysis, radiolysis, sonochemistry and thermolysis reduction [12]. The most popular method is based on the reduction of tetrachloroauric acid by traditional reducing agent (e.g. NaBH₄) in the presence of thiol-functionalized chemical species as protecting agent [13,14]. However, thiol-modified surface can be destroyed by exposing to light, high temperature and oxygen [15,16]. A convenient preparation method has been reported that colloidal stable gold nanoparticles can be formed in a single step by certain polymers, which serve as both the reducing agent and the stabilizer [17–20]. Such an approach greatly simplified the preparation and purification of gold nanoparticles. Several groups have reported the *in situ* preparation of gold nanoparticles using poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA)-based linear block copolymers [17,18], poly(amidoamine) dendrimers [19] and poly(propyleneimine) dendrimers [20] as reducing agent and stabilizer. Previous studies also showed that the architecture of polymer acting as stabilizer was related with the properties of inorganic nanoparticles [5,18,19]. Qi et al. prepared CdS nanoparticles using linear and branched poly(ethylene glycol)-*b*-poly(ethyleneimine) and PEG-Starburst as

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stabilizer, respectively [5]. It was found that a polymer with an optimum of an effective functional group accessibility between molecular flexibility and functional group density will be more effective in controlling the particle size and the polymer with branched structure is endowed with this merit since the local concentration of basic nitrogens in linear PEI block is lower than that on the branched PEI block and PEG-Starburst possesses lower accessibility of all amine groups in the more regular dendrimer structure compared to the branched PEI. Thus, the studies on the preparation of gold nanoparticles using graft copolymer as reducing agent and stabilizer can provide more information about the correlation between the structure of copolymer and the properties of gold nanoparticles.

In this work, we reported the preparation of colloidal stable gold nanoparticles with controllable size and remarkable stability (at least 2 months) using poly(*N*-isopropylacrylamide)-*b*-[poly(ethyl acrylate)-*g*-poly(2-(diethylamino)ethyl methacrylate)] (PNIPAM-*b*-(PEA-*g*-PDEAEMA)) as reducing agent and stabilizer (Scheme 1). PDEAEMA is selected as side chains since it can reduce AuCl₄⁻ to zerovalent gold without external reducing agent and multi-point coordination of tertiary amino groups of PDEAEMA on the surface of gold can lead to efficient interaction between PDEAEMA and gold, which will facilitate the preparation of stable colloidal stable gold nanoparticles [18]. PNIPAM segment is able to provide a highly hydrated, adsorbed layer to enhance the stability of gold nanoparticles [18,21]. The compact structure of graft copolymer linked by stable covalent bonds expected to stabilize nanoparticles and prevent the unfavorable aggregation since that side chains can protect the formed single particle [22]. The results of ultraviolet visible absorption spectroscopy (UV-vis) and transmission electron microscopy (TEM) demonstrated the preparation parameters can effectively influence the morphology and size of gold nanoparticles.

2. Experimental part

2.1. Materials

Tetrachloroauric acid trihydrate (HAuCl₄·3H₂O, Aldrich, 99%) were used as received. The synthesis and characterization of PNIPAM-*b*-(PEA-*g*-PDEAEMA) double hydrophilic graft copolymers were reported in an earlier publication [23]. Data of molecular weight, molecular weight distribution, composition

Table 1
Structure parameters of PNIPAM-*b*-(PEA-*g*-PDEAEMA) graft copolymers.

Sample	M_n^a (kDa)	M_w/M_n^a	$N_{\text{DEAEMA}}/N_{\text{NIPAM}}/N_{\text{HEA}}^b$	n_{DEAEMA}^c
1a	54.9	1.37	331/144/37	8.9
1b	78.1	1.35	648/144/37	17.5
1c	87.7	1.25	907/144/37	24.5
1d	96.0	1.30	1022/144/37	27.6
1e	112.6	1.26	1440/144/37	38.9

^a Measured by GPC in THF.

^b The numbers of DEAEMA, NIPAM and HEA repeating units obtained by ¹H NMR and GPC/MALS.

^c The number of DEAEMA repeating unit per side chain.

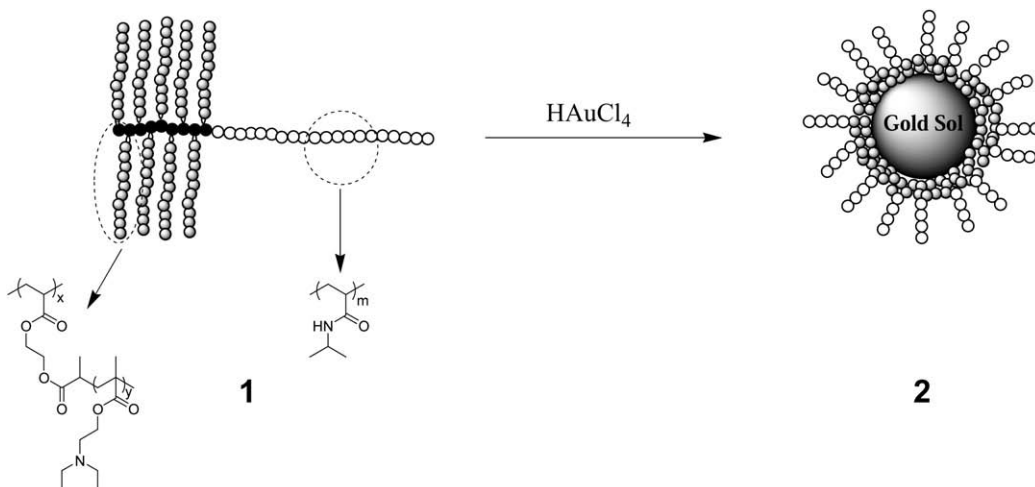
and the length of PDEAEMA side chains of each sample are summarized in Table 1.

2.2. Measurements

UV-vis spectra were recorded for dilute aqueous dispersions of gold nanoparticles in a quartz cuvette (1 cm × 1 cm) by a Varian Cary 300 spectrophotometer. TEM images were obtained by a Philips CM120 instrument operated at 80 kV. 10 μL aqueous solution of gold nanoparticles was deposited on an electron microscopy copper grid coated with carbon film and water evaporated at room temperature. The number-averaged diameter of gold nanoparticles was estimated by counting the sizes of more than 200 nanoparticles from TEM images [18]. X-ray diffraction (XRD) measurement was taken to investigate the crystal structure of gold nanoparticles by a Philips X'Pert PRO X-ray powder diffractometer with CuKα (1.541 Å) radiation (40 kV, 40 mA) and the sample was exposed at a scan rate of $2\theta = 0.0334^\circ/\text{s}$ in the range between 30° and 85°. Hydrodynamic diameter (D_h) and zeta potential were measured by a Malvern Nano-ZS90 Zetasizer. AFM image was performed by a Veeco Nanoscope IV-MultiMode microscope. 10 μL aqueous solution of gold nanoparticles **2d** was deposited on a piece of freshly cleaved mica and water evaporated at room temperature; AFM image was obtained with tapping mode using standard Si probe.

2.3. Preparation of gold nanoparticles 2

Various amounts of aqueous solution of HAuCl₄ were added into aqueous solution of PNIPAM-*b*-(PEA-*g*-PDEAEMA) **1** graft



Scheme 1. Preparation of size-controllable stable colloidal gold nanoparticles via PNIPAM-*b*-(PEA-*g*-PDEAEMA) double hydrophilic graft copolymer.

copolymers to prepare copolymer-stabilized gold nanoparticles. In a typical procedure, 200 μL THF solution of **1d** (20 mg/mL) was added to 8 mL of acidified deionized water with a pH value of 4.0 ($[\text{DEAEMA}] = 2.4 \times 10^{-3}$ mol/L) and the solution was stirred for several hours for the evaporation of THF. Next, 60 μL of aqueous solution of HAuCl_4 (2.4×10^{-2} mol/L) was charged and dilute HCl was introduced to adjust pH of the solution to 5.5. The reaction mixture was stirred at 20 $^\circ\text{C}$ in darkness for 48 h and pH of the solution turned to 5.8.

3. Results and discussion

3.1. Preparation and characterization of copolymer-stabilized gold nanoparticles

In our preliminary control experiments, the formation of gold nanoparticles was examined in the existence of PNIPAM homopolymer ($M_n = 4100$, $M_w/M_n = 1.03$) synthesized by single-electron-transfer living radical polymerization (SET-LRP). A 200 μL of THF solution of PNIPAM homopolymer ($[\text{polymer}] = 11$ mg/mL) was added to 8 mL of deionized water and the solution was stirred for several hours for the evaporation of THF. Next, 60 μL of aqueous solution of HAuCl_4 (2.4×10^{-2} mol/L) was added and pH of the solution was adjusted to 5.5. After the solution was stirred at 20 $^\circ\text{C}$ in darkness for 48 h, we cannot find any absorbance trace around 530 nm in UV-vis spectrum, indicating PNIPAM chain was not able to reduce AuCl_4^- to zerovalent gold. In contrast, the solution gradually turned from colorless to pink after several hours with stirring using PNIPAM-*b*-(PEA-*g*-PDEAEMA) **1d** instead of PNIPAM at the same condition. The maximum absorption wavelength of UV-vis spectrum located at 523 nm, which corresponded to the surface plasmon absorption of gold nanoparticles. The size and shape of gold nanoparticles were examined by TEM. A spherical morphology was observed with a diameter ranging from 2.6 nm to 13.5 nm and the number-averaged diameter was estimated to be 6.6 ± 1.8 nm as listed in Table 2. This result verifies PDEAEMA can serve as an effective reducing agent to reduce AuCl_4^- to zerovalent Au by the amine groups followed by resulting in the formation of gold nanoparticles [20,24]. On the other hand, multi-point coordination of tertiary amino groups leads to efficient interaction between PDEAEMA and Au and PNIPAM segment can provide a highly hydrated, adsorbed layer facilitating the preparation of stable colloidal gold nanoparticles [18,21].

PNIPAM-*b*-(PEA-*g*-PDEAEMA) **1** graft copolymers were mixed with HAuCl_4 in darkness to prepare gold nanoparticles. The maximum absorption wavelengths of all gold sols are found to be between 521 nm and 534 nm (Table 2), denoting the surface plasmon absorption of gold nanoparticles. X-ray diffraction measurement of sample **2d** was conducted to further confirm the formation of gold nanoparticles (Fig. 1). We can find five prominent characteristic peaks ($2\theta = 38.3^\circ$, 44.3° , 64.8° , 77.9° and 81.8°), which are

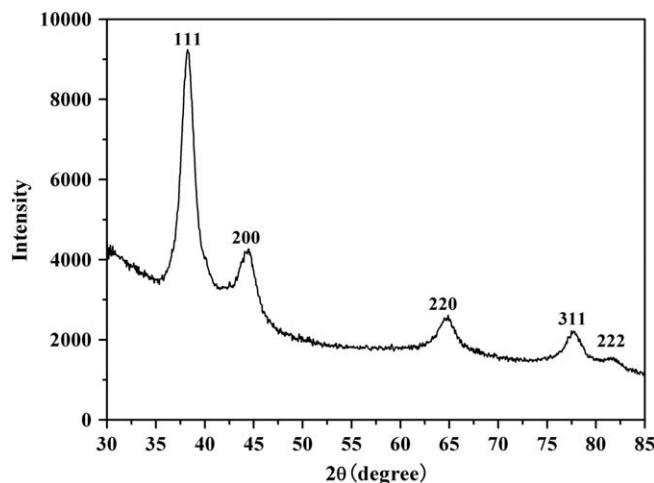


Fig. 1. XRD pattern of gold nanoparticles **2d**.

attributed to (111), (200), (220), (311) and (222) Bragg reflections of the face-centered cubic (fcc) structure of gold metal, respectively [25]. An average crystallite size can be evaluated from the XRD pattern by Debye-Scherrer formula $D_{hkl} = k\lambda/\beta \cos \theta$, in which D_{hkl} is the particle size parallel to (hkl) plane, k is a geometrical constant with a typical value of 0.89 for spherical particles, λ is the wavelength of the radiation, β is the full width at half maximum (FWHM) in radiations and θ is the position of the diffraction peak. The grain size is calculated to be 5.8 nm from the strongest peak (111), which is comparable to the statistical result (6.6 nm) obtained from TEM.

Zeta potential measurement shows that the surface charge of **2d** is 48.5 ± 2.7 mV when pH = 5.8 (Fig. 2A), which evidences the absorption of positively charged PDEAEMA segment onto gold nanoparticles [6,26]. Dynamic light scattering study on **2d** indicates an intensity-average diameter of 57.8 ± 11.2 nm (Fig. 2B), which is much larger than the value obtained by TEM (6.6 ± 1.8 nm). This phenomenon might be explained by two causes: firstly, TEM is only sensitive to the electron-rich metal particle, whereas DLS acquires the size of whole gold-copolymer composite nanoparticles including the hydrated layer of graft copolymer that is adsorbed onto the surface of the gold nanoparticles [18,27]; secondly, allowing for the polydispersity effects, DLS is sensitive to the larger particles in the size distribution.

Fig. 3 show AFM height and phase images of gold nanoparticles **2d**. The average diameter of gold nanoparticles **2d** obtained from AFM is 40.0 ± 6.8 nm (Fig. 3A), which is smaller than the value given by DLS. DLS offers the dimension of nanoparticles with hydrated layer of graft copolymers, whereas AFM reflects the conformation of nanoparticles in dry state. Therefore, the deformation and collapse of the layer of graft copolymer induce a smaller size. Owing to the strong phase contrast given by opposite (hard and soft) viscoelastic behaviors of the surface components, tapping phase mode analyses (recording the shift of the tip vibration phase angle induced by the interactions with the sample surface) are likely to give suitable images of the surface rigidity differences, and then of the composition of the sample surface layers [28]. It is obvious that the contrast gives a relative difference between the hard and soft domains as shown in Fig. 3B. It can be assumed that these heterogeneities correspond to “harder” domains of gold nanoparticles coated with a layer of a “softer” matrix of graft copolymers. From the above results, we can conclude that gold nanoparticles were successfully prepared via PNIPAM-*b*-(PEA-*g*-PDEAEMA) **1** double hydrophilic graft copolymer.

Table 2
Gold nanoparticles stabilized by PNIPAM-*b*-(PEA-*g*-PDEAEMA) **1**.^a

Entry	Polymer	$[\text{DEAEMA}]/[\text{Au}^{3+}]$	λ_{max}^b (nm)	Particles size ^c (nm)
2a	1a	13.3/1	534	16.2 ± 3.1
2b	1b	13.3/1	527	11.3 ± 4.1
2c	1c	13.3/1	523	6.8 ± 2.2
2d	1d	13.3/1	523	6.6 ± 1.8
2e	1e	13.3/1	521	5.7 ± 1.3

^a $[\text{DEAEMA}] = 2.4 \times 10^{-3}$ mole/L.

^b Measured by UV-vis.

^c Obtained by counting the sizes of more than 200 nanoparticles from TEM image.

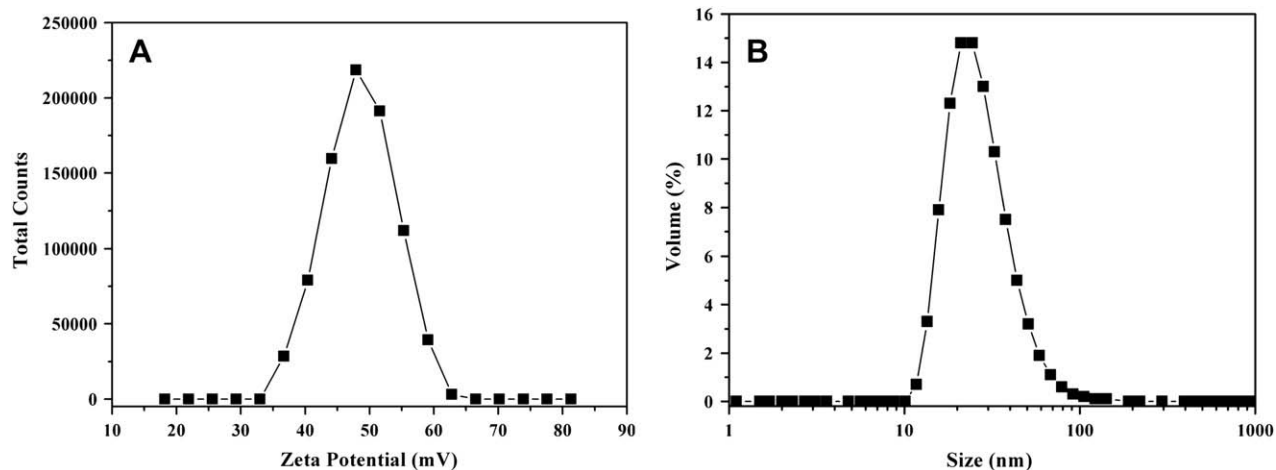


Fig. 2. (A) Zeta potential of gold nanoparticles 2d at pH = 5.8; (B) Hydrodynamic diameter distribution of gold nanoparticles 2d.

3.2. Influence of length of side chains on formation of gold nanoparticles

Previous studies showed that the architecture of polymer was related with the properties of gold nanoparticles [18,19]. To examine the effect of the length of PDEAEMA segment on the formation of gold nanoparticles, five graft copolymer samples with different length of PDEAEMA side chains (**1a–1e** as listed in Table 1) were used to prepare gold nanoparticles. Fig. 4A shows UV–vis spectra of gold nanoparticles **2**. Data of maximum absorbance wavelength of plasmon resonance (Table 2) illustrated that the decreasing of the length of PDEAEMA side chains results in a red-shift of the plasmon absorption band, which means an increase in particle size.

The morphology of gold nanoparticles **2** are visualized by TEM as shown in Fig. 4B–F. Gold nanoparticles stabilized by graft copolymers **1c**, **1d** and **1e** have spherical morphology with the number-average diameters of 6.8 ± 2.2 nm, 6.6 ± 1.8 nm and 5.7 ± 1.3 nm, respectively. In contrast, gold nanoparticles **2a** and **2b**, which were prepared by employing graft copolymers **1a** and **1b** with shorter PDEAEMA side chains, have larger sizes and much broader size distributions (Fig. 4B and C). This phenomenon is consistent with the red-shift appeared in UV–vis spectra. Moreover, the shape of gold nanoparticles **2a** and **2b** are spheres and ill-

defined spheres. Esumi et al. have found that poly(amidoamine) dendrimers of earlier generation could not give effective protective gold nanoparticles, whereas the dendrimers of later generation provided an effective action in preparing gold nanoparticles with smaller size and narrower size distribution due to their closed and compact structure as the increasing of the generation [19]. The structure of graft copolymers will become more closed and compact with the increasing of the length of side chains, which means that graft copolymers with longer side chains possess more effective action, that is, the graft copolymers with longer side chains have more capacity to envelop the growing colloids [29]. On the other hand, Alexandridis et al. have pointed out that the competition between the reaction activity induced by PEO-*b*-PPO-*b*-PEO and the adsorption of block copolymer determines the size of gold nanoparticles prepared by using PEO-*b*-PPO-*b*-PEO as reduction agent and stabilizer and the covering of block copolymers on the surface of gold nanoparticles restricted the final particle size [30]. In current case, the concentrations of DEAEEMA in all five solutions are same, indicating the reaction activities are supposed to be equal. However, the capacity of graft copolymer to envelop the gold nanoparticles would be enhanced as the length of PDEAEMA side chains increases from 8.9 units to 38.9 units. Thus, the side-chain-length effect will become more pronounced for determining the particle size. The number-averaged diameters of

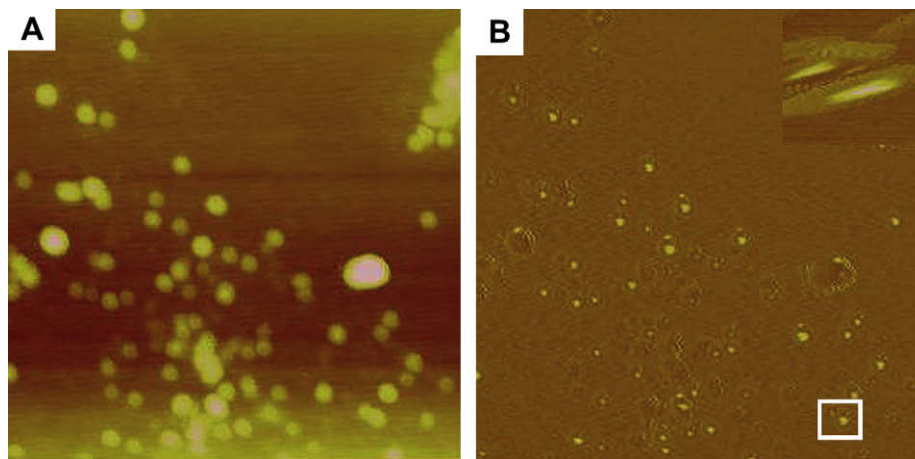


Fig. 3. AFM height and phase images of gold nanoparticles 2d: (A) height image (vertical gray scale: 20 nm); (B) phase image (vertical gray scale: 90°). Inset of part (B) shows a magnified version of the area with the white square.

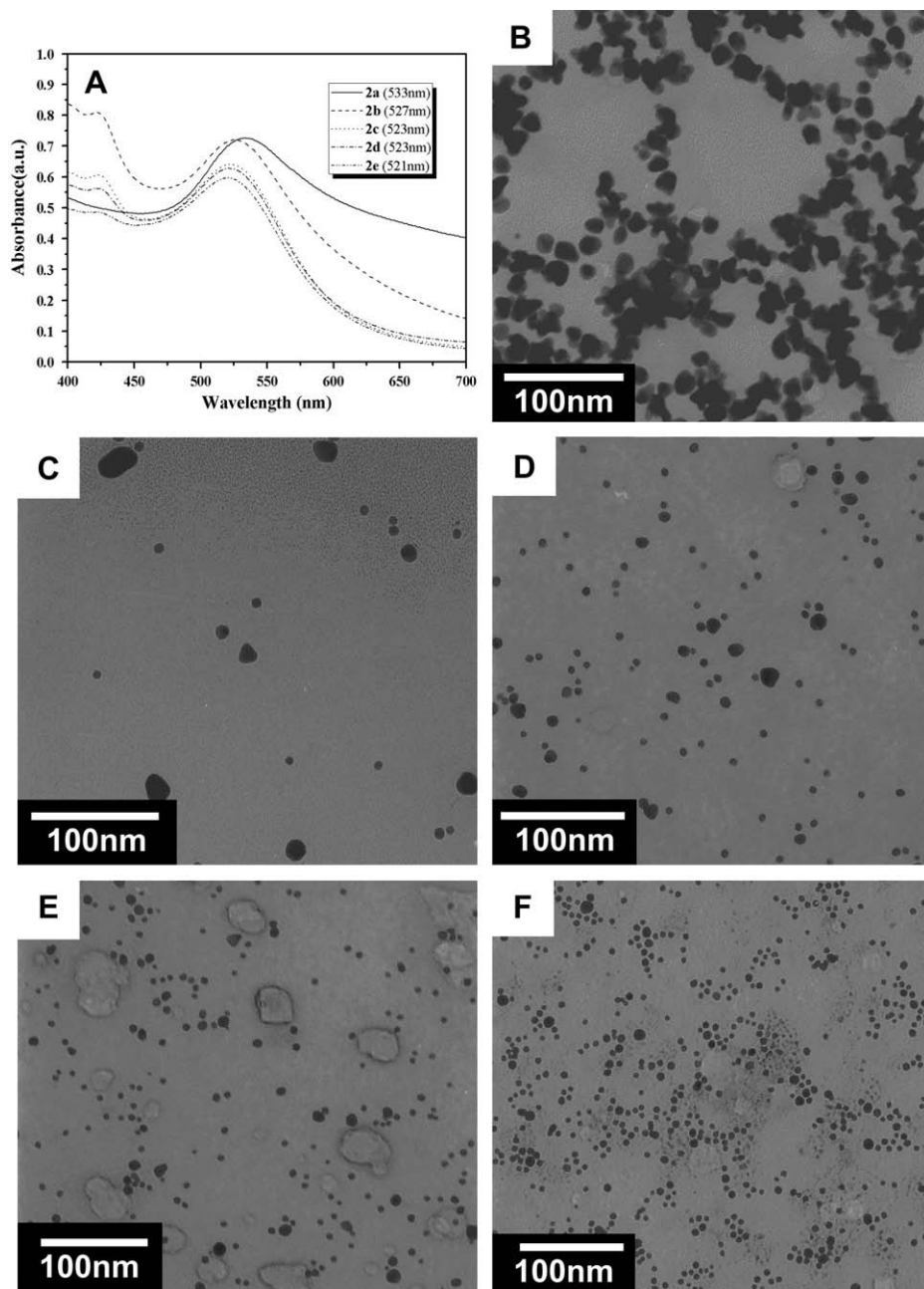


Fig. 4. Gold nanoparticles stabilized by PNIPAM-*b*-(PEA-*g*-PDEAEMA) 1 graft copolymers with variable lengths of PDEAEMA side chains. (A) UV-vis absorption spectra of gold nanoparticles 2; representative TEM images of gold nanoparticles 2 stabilized by 1a (B), 1b (C), 1c (D), 1d (E) and 1e (F).

gold nanoparticles show a monotonous decreasing tendency from 16.2 nm to 5.7 nm as expected while the length of PDEAEMA side chains ascended from 8.9 units to 38.9 units (Table 2), implying the number-averaged size of gold nanoparticles 2 can be tuned by the length of PDEAEMA side chains.

3.3. Effect of $[DEAEMA]/[AuCl_4^-]$ molar ratio on formation of gold nanoparticles

Four different $[DEAEMA]/[AuCl_4^-]$ molar ratios (Table 3) were used in preparing gold nanoparticles stabilized by PNIPAM-*b*-(PEA-*g*-PDEAEMA) 1b. The maximum absorption wavelength of gold sol shows a red-shift from 520 nm to 534 nm with the increasing of $[DEAEMA]/[AuCl_4^-]$ molar ratio, indicating a notable enlarging in the size of gold nanoparticles. Gold nanoparticles were found to

have larger diameters and broader size distributions with $[DEAEMA]/[AuCl_4^-]$ molar ratios of 26.6/1 and 13.3/1 (Fig. 5A and B), which agreed with the red-shift appeared in UV-vis spectra. In contrast, gold nanoparticles prepared with lower $[DEAEMA]/$

Table 3
Effect of $[DEAEMA]/[AuCl_4^-]$ on the formation of gold nanoparticles^a

Entry	Polymer	$[DEAEMA]/[AuCl_4^-]$	λ_{max} (nm) ^b	Particle size ^c (nm)
2f	1b	26.6/1	534	14.1 ± 3.4
2b	1b	13.3/1	527	11.3 ± 4.1
2g	1b	6.7/1	522	7.4 ± 3.5
2h	1b	3.3/1	520	5.6 ± 1.1

^a $[DEAEMA] = 2.4 \times 10^{-3}$ mole/L.

^b Measured by UV-vis.

^c Obtained by counting the sizes of more than 200 nanoparticles from TEM images.

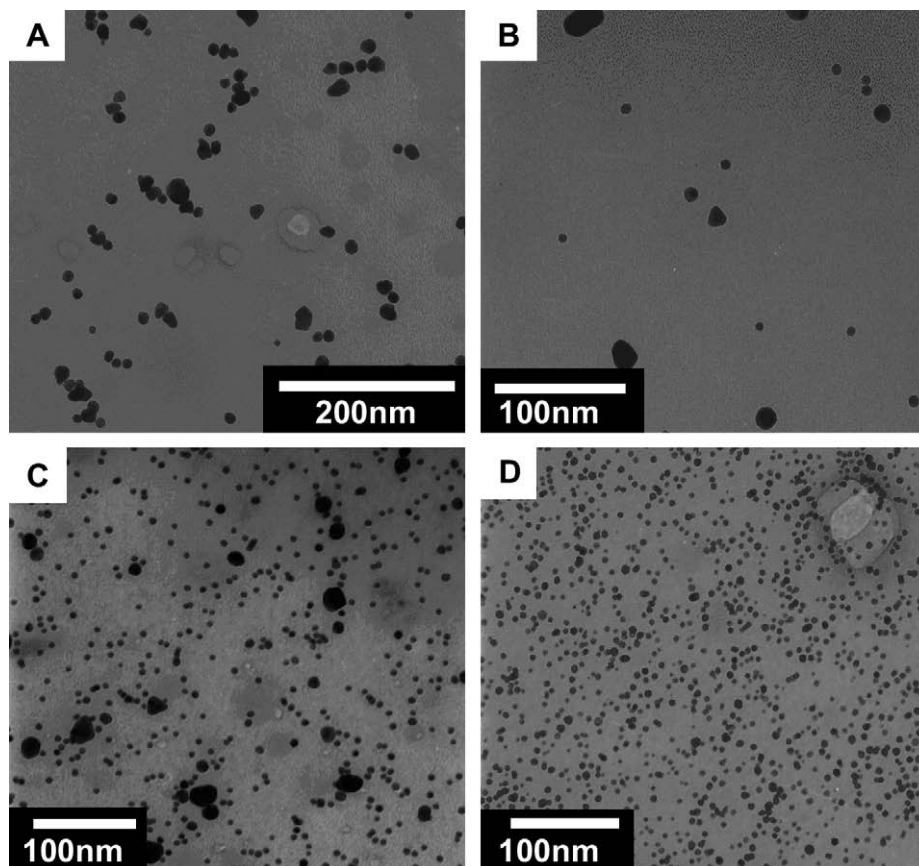


Fig. 5. TEM images of gold nanoparticles 2 prepared by employing 1b at [DEAEMA]/[AuCl₄⁻] molar ratio of (A) 26.6/1; (B) 13.3/1; (C) 6.7/1 and (D) 3.3/1.

[AuCl₄⁻] molar ratio of 3.3/1 have a smaller diameter and narrower size distribution of 5.6 ± 1.1 nm (Fig. 5D).

The size of gold nanoparticles has been reported to be strongly affected by the relative and absolute concentrations of HAuCl₄ and polymer [18,30]. Armes et al. have reported that lower [copolymer]/[HAuCl₄] gave a smaller size of gold nanoparticles employing PDMAEMA-based linear block copolymer as reduction agent and stabilizer [18]. Furthermore, previous studies showed that particle size was determined by the competition between the reaction activity and the absorption of copolymer [30]. In current case, the increase of [DEAEMA]/[AuCl₄⁻] molar ratio resulted in the increasing of the reaction activity and the enhancement of the absorption of copolymers. The increase of the reaction activity will facilitate the formation of gold nanoparticles with a larger size whereas the enhancement of the absorption limited the particle growth [30]. Thus, the influence of [DEAEMA]/[AuCl₄⁻] molar ratio on the size of gold nanoparticles depends on which effect is dominant. In this study, the number-averaged size of gold nanoparticles shows a monotonous decreasing tendency from 14.1 nm to 5.6 nm with the decreasing of [DEAEMA]/[AuCl₄⁻] molar ratio from 26.6/1 to 3.3/1 (Table 3). It is clear that a higher concentration in AuCl₄⁻ results in a smaller size of gold nanoparticles. Therefore, the effect of reaction activity can be supposed to be the main factor of affecting the particle as [DEAEMA]/[AuCl₄⁻] molar ratio varies and the size of gold nanoparticles also can be regulated by [DEAEMA]/[AuCl₄⁻] molar ratio. It is necessary to point out that gold nanoparticles stabilized by PNIPAM-*b*-(PEA-*g*-PDEAEMA) graft copolymers show a remarkable colloidal stability without any observable flocculation or aggregation for at least 2 months, which confirmed that PNIPAM-*b*-(PEA-*g*-PDEAEMA) graft copolymer is a kind of

effective stabilization agent due to the compact structure of graft copolymer and the presence of side chains for protecting the formed single particle.

4. Conclusions

In summary, PNIPAM-*b*-(PEA-*g*-PDEAEMA) double hydrophilic graft copolymers can be employed to prepare high-quality gold nanoparticles in aqueous media without any external reducing agent. The average size can be controlled by varying the length of PDEAEMA side chains and [DEAEMA]/[AuCl₄⁻] molar ratio. Moreover, PDEAEMA is a kind of weak cationic pH-responsive polyelectrolyte which will allow for the conjugation with other functional molecules or polymers by electrostatic interactions to fabricate multi-functional nanomaterials.

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