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One-step method for preparation of pH-responsive gold nanoparticles with block copolymer shell structures by UV irradiation

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Abstract Gold nanoparticles (AuNPs) are synthesized by UV irradiation of the solution of poly(2-vinyl pyridine)-*block*-poly(ethylene oxide)/$HAuCl_4$ (PVP-*b*-PEO/$HAuCl_4$) complexes. The AuNPs with cross-linked copolymer shells are stable in organic solvents and various biochemical buffers. It is found that AuNPs are pH sensitive. The average hydrodynamic diameter (D_h) of the AuNPs in water measured by dynamic light scattering (DLS) is affected by the pH value of buffers. The optical properties of the AuNPs are also sensitive to the solution pH due to structural changes of the copolymers. It is expected that AuNPs will be useful as plasmonic, light-scattering, and light-absorbing analogs.

Keywords Block copolymer · Gold nanoparticles · UV irradiation · pH sensitivity

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Introduction

Gold nanoparticles (AuNPs) have been intensively investigated by the biomedical research community due to their potential applications as disease detection sensors [1], drug delivery vehicle [2], and imaging contrast agents [3]. However, they are usually bioincompatible, unstable and highly toxic to living cells and tissues. To improve colloidal stability, biocompatibility and the properties of response of AuNPs under physiological conditions, many investigations have been done on functionalizing AuNPs [4–10].

Thiol chemistry has widely been used to modify the surface of AuNPs with synthetic polymers and biomacromolecules [11–17]. Conjugation of appropriately chosen signaling molecules is used to control the interaction of AuNPs with a desired target [18–20], affording functional AuNPs that specifically interact with proteins [21], nucleic acids [22], and/or other nanoparticles [23]. However, the functionality of thiolate-modified AuNPs in vivo is limited to only a few days because of the limited oxidative stability of thiolate species as well as exchange reactions with thiolated compounds inside the body. Thiolate-modified surfaces are also damaged by exposure to light, high temperature, and oxygen [24–26]. To overcome the drawbacks, AuNPs encapsulated by a functional polymeric chain have drawn a lot of attention [27–31]. For example, amphiphilic or pH-responsive AuNPs can be obtained by linking a polymer chain to the surface of AuNPs [32, 33].

The utilization of block copolymer micelles for the synthesis and stabilization of aggregation-free AuNPs has been reported with different polymer systems, such as poly(styrene-*block*-ethylene oxide) (PS-*b*-PEO), poly(styrene-*block*-vinyl pyridine) (PS-*b*-PVP), and poly(styrene-*block*-acrylic acid) (PS-*b*-PAA) [2, 34–41]. To enhance the stability of the surfactant layer of AuNPs, chemical cross-linking the surfactant molecules has been investigated [37–41]. For example, PS-*b*-PAA and PMMA-*b*-PAA were used as encapsulating amphiphiles, and the hydrophilic PAA block of the assembled polymer layer was crosslinked using aqueous carbodiimide/diamine coupling [42]. However, the density of crosslinks in the assembled shell was low. As a result, while the stability of the particles was enhanced by PAA-cross-linked surfactants, the particles still did not survive in the conditions of harsher biotechnological protocols (e.g., high-temperature methods involving thermophile enzymes) [40].

Photochemistry as a green synthesis method can improve the quality of AuNPs due to its simplicity, reproducibility, and mild synthesis conditions [43, 44]. AuNPs synthesized under ultraviolet (UV) light irradiation have been reported in the presence of polymethylmethacrylate, hexadecyltrimethylammonium chloride, sodium alginate, chitosan, and cetyltrimethylammonium chloride [45–49]. Yu et al. reported synthesis of water-dispersed, polymer-stabilized AuNPs by UV irradiation-enhanced reduction in the presence of double hydrophilic block copolymers with different functional patterns [50]. Chen reported one method for the photoencapsulation of AuNPs using premade AuNPs and photo-cross-linkable block copolymer amphiphiles [polystyrene-*co*-poly(4-vinyl benzophenone)]-*block*-poly(acrylic acid) or [poly(styrene)-*co*-poly(4-vinylbenzophenone)]-*block*-poly(ethylene oxide) [40]. UV irradiation led to photochemical crosslinking the poly(styrene)-*co*-poly(4-vinylbenzophenone) cores. The cross-linked polymer shells can improve the stability of nanoparticles in both organic solvents and biochemical buffers [40].

It is well known that PEO is a water-soluble polymer. PVP is protonized and soluble in acid solutions at lower pH, whereas the deprotonized PVP that exists at higher pH is water insoluble. Therefore, AuNPs with PVP-*b*-PEO shells may exhibit some attractive properties, including their solubility in water, pH sensitivity, the temperature sensitivity, resistance of the PEO shell to protein adsorption and cellular adhesion [51].

Here, we report a simple method to produce AuNPs with a response to pH. Our method is to prepare AuNPs with block copolymer shells in one-step synthesis by UV irradiation of the solution of the PVP-*b*-PEO/$HAuCl_4$ complexes. The AuNPs with block copolymer shells can easily be re-dispersed into water or organic solvents, such as ethanol, THF, DMF, etc. Specially, the resultant AuNPs are stable enough to remain suspending in buffers for 24 h. It is found that the AuNPs are pH responsive, the diameters and the UV-adsorption peaks of AuNPs is affected by the pH value.

Experimental part

Materials

PVP-*b*-PEO was purchased from Polymer Source Inc., Dorval, QC, Canada. The molecular weight of the PVP block was 3,000 and of the PEO block 10,000, M_w/M_n was 1.13. The volume fraction of the PVP block in the copolymer is 0.23. Tetrachloroauric (III) acid ($HAuCl_4 \cdot xH_2O$, $M_w = 333.79$) and 2,4-dihydroxy benzophenone (BPH, 99%) were purchased from Alfa Aesar and used as received. Anhydrous tetrahydrofuran (99.9%) was purchased from Sigma-Aldrich.

Sample preparation

Given amounts of PVP-*b*-PEO, $HAuCl_4$, and BPH (2.0 wt%, relative to the PVP-*b*-PEO block copolymer) were dissolved together in THF at about 36 °C and stirred overnight to make a homogeneous solution. The solution was transferred into quartz flasks and irradiated with UV light for 16 h in a reactor equipped with a 30 W lamp (Spectronics Co., USA) of wavelength 254 nm.

Characterization

UV–vis spectra of the UV-exposed solutions were recorded on a UV2450 spectrometer (Shimadzu Co., Japan). Dilute solutions of the AuNPs were measured in quartz cuvettes, using pure solvent as a reference. Electron micrographs of the particles were taken with an H-800 transmission electron microscope (Hitachi, Japan), operating at 100 kV. High-resolution TEM (HRTEM) measurements were performed on a JEM-2100 electron microscopy (JEOL Ltd., Japan) operating at 200 kV. The samples were prepared by mounting a drop of the AuNPs solution on a carbon-coated Cu grid and allowing it to dry in air. Dynamic light scattering (DLS) measurements were measured with a Zetasizer 3000HS (Malvern Instruments, Ltd., UK). A He–Ne laser with a wavelength of 632.8 nm was used. The temperature was set to 25 °C and the angle measurement was 90°. Thermogravimetric analyses were performed with a Diamond TG/DTA instrument (Perkin-Elmer, USA). Pure PVP-*b*-PEO copolymer and the UV-irradiated sample were heated in nitrogen from 100 to 800 °C at a heating rate of 10 °C min^{-1}.

Stability in buffer

AuNPs with copolymer shells were dialyzed against buffers, including citric acid buffers (10 mM, pH 3, 4, 5, and 6), Tris buffer (10 mM, pH 7.0), carbonate buffer (25 mM, pH 10.5), and phosphate buffer (0.1 M, pH 7 and 8). The UV–vis spectra of these suspensions were measured after 24 h to evaluate stability, and particle sizes were measured at different pH values by DLS.

pH-Dependent investigations of AuNPs

A 20 mL aliquot of AuNPs was transferred to a glass container and adjusted to the appropriate pH by adding either 1.0 M HCl or 1.0 M NaOH solution with constant stirring until the pH was stable. The solution was then stirred for another 30 min before analyzing by UV spectroscopy.

Results and discussion

Photoencapsulation of Au nanoparticles

In this work, one-step process was used to prepare water soluble, pH-sensitive AuNPs with cross-linkable PVP-*b*-PEO shells. $HAuCl_4$ precursors and PVP-*b*-PEO block copolymers were dissolved together in THF, and then the mixture solution was irradiated with UV light for 16 h. As shown in Fig. 1, the DLS results reveal that PVP-*b*-PEO molecules are present as unimers of about 6 nm in diameter. Addition of $HAuCl_4$ to the PVP-*b*-PEO solution results in the increase of the hydrodynamic size of PVP-*b*-PEO copolymers to about 12 nm. The increase of the size is attributed to the decrease of the solubility of PVP in THF after the complexation between $HAuCl_4$ and the pyridine units [36]. When a mixture solution of 0.05 wt% (the loading ratio of $HAuCl_4$/VP is 0.1) was irradiated with UV light, the color of the solution turned from light yellow to ruby red, indicating the formation of AuNPs, and the hydrodynamic size of the AuNPs is about 40 nm. TEM image shown in Fig. 2a illustrates that the drying AuNPs of ~18 nm in diameter are covered by PVP-*b*-PEO copolymer shells, which is smaller than that of the value measured by DLS in solution. The HRTEM image inserted in Fig. 2a reveals that the AuNPs are crystalline. The UV–vis absorption band corresponding to the surface plasmon resonance (SPR) energy of the core–shell nanoparticles is 532 nm (Fig. 2c). It is found that if the resulting AuNPs are dried and re-dispersed in water, the SPR peak is shifted to 525 nm, which are attributed

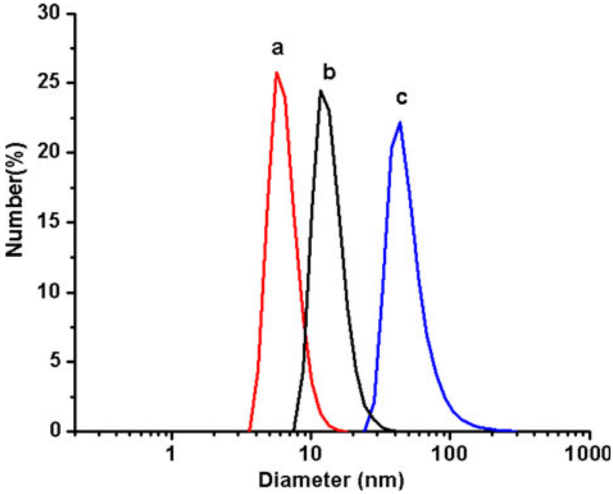


Fig. 1 DLS results of (*a*) PVP-*b*-PEO/THF solution (0.5 wt%), (*b*) PVP-*b*-PEO/$HAuCl_4$ (0.1)/THF solution (0.5 wt%), and (*c*) AuNPs prepared by irradiating a 0.5 wt% PVP-*b*-PEO/$HAuCl_4$ (0.1)/THF solution for 16 h

to the response of the SPR to the refractive index of the particles' local environment [52]. AuNPs can be re-dispersed in water, indicating that the Au cores are surrounded by the copolymer chains and the outer layer of a shell is composed of water-soluble PEO blocks. To further prove that the surfaces of AuNPs were covered by PVP-*b*-PEO copolymers, a film was prepared by spin coating the AuNPs/THF solution on a silicon substrate and the contact angle of the film was measured (Fig. 2d–e). The contact angle of the film (~43°) is smaller than those of the silicon substrate (~56°), the pure PVP film (~68°) and the ultrasmooth gold surfaces (~71°) [53]. It is reasonable to deduce that the outer layer and the inner layer of a shell are composed of PEO and PVP blocks.

The experiments were carried out in the presence of 2, 4-dihydroxybenzophenone. The mechanism of benzophenone cross-linking reaction in polymeric and micellar systems was understood by Matsukuma [54] and others [55–58]. It has been reported that PEO and PVP can be crosslinked during UV irradiation process, and pH-sensitive hydrogel can be obtained by crosslinking of PEO and PVP blends with UV radiation [59]. We prepared AuNPs with PS-*b*-PVP shells by UV irradiation and demonstrated that the PS-*b*-PVP copolymer shells were crosslinked [53]. To prove that the PVP-*b*-PEO copolymers were crosslinked during UV irradiation process, TGA analyses of the pure copolymer, and the UV-irradiated sample were performed (Fig. 3). The main weight loss for both samples takes place in the temperature range of 230–400 °C. The complete decomposition temperature of the UV-irradiated sample is higher than that of the pure copolymer sample. The thermal stability of the block copolymers is improved, which illustrates that the copolymers are crosslinked after UV irradiation. The formation process of the AuNPs with PVP-*b*-PEO shell structures may be understood as follows. During the UV irradiation process, BPH undergoes several photophysical processes, affording an n, π^* triplet state which then proceeds to reduction of BPH and copolymer

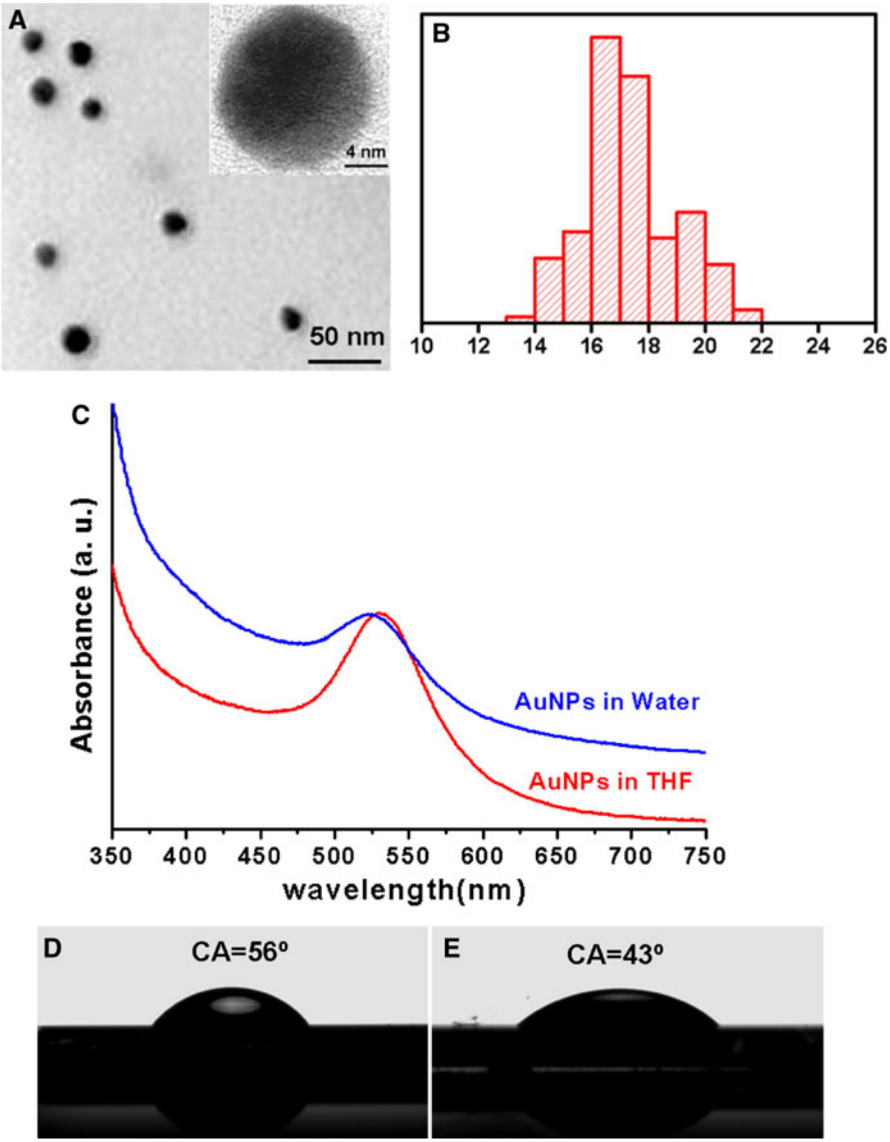


Fig. 2 TEM and HRTEM images of the core–shell AuNPs (**a**), size distribution of the AuNPs (**b**), UV–vis spectrum of AuNPs in THF and water (**c**). The sample was prepared by irradiating a 0.5 wt% PVP-*b*-PEO/$HAuCl_4$ (0.1) THF solution for 16 h. The contact angles of silicon substrate (**d**) and the AuNPs film (**e**)

radical formation [60]. Reduction of $HAuCl_4$ to Au and photochemical cross-linking of the block copolymers chains take place simultaneously (Scheme 1). Photo-cross-linking occurs mainly by recombination reaction of two copolymer radicals producing carbon–carbon bonds between the main chains. The cross-linking reaction of PVP or PEO blocks leads to the formation of a copolymer shell. The

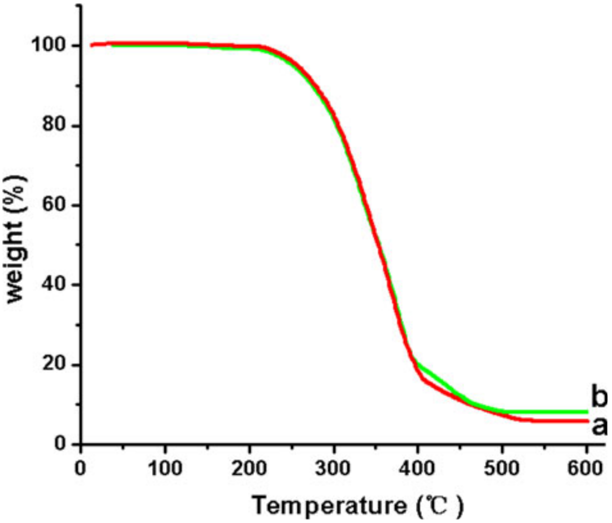


Fig. 3 TGA curves of pure copolymers (*a*) and the UV-irradiated copolymer sample (*b*)

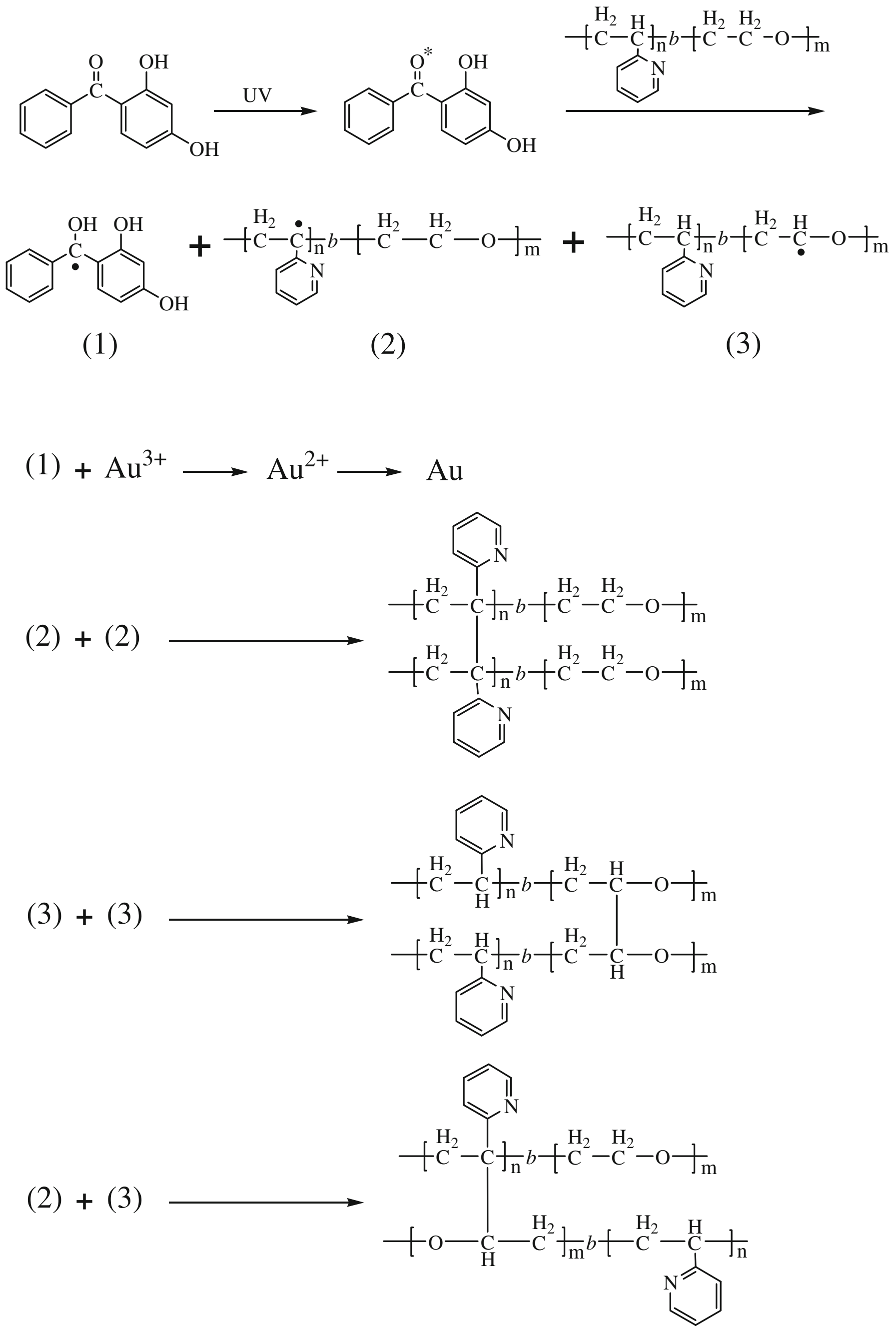
formed metallic Au atoms are forced to aggregate to form the core. Due to the preferential interactions between pyridine units and Au, the inner layer and the outer layer of a shell are mainly composed of PVP and PEO block chains, respectively.

Stability of AuNPs with copolymer shells in various media

For applications in optical-based sensors, it is important to investigate the stability of the AuNPs at different pH buffers. It is found that PVP-*b*-PEO copolymer shells improved the suspension and stability of the AuNPs in a variety of environments, including organic solvents, water, and commercially available buffers. When AuNPs were transferred to water and dialyzed against buffers, including Tris buffer (10 mM, pH 7.19), carbonate buffer (25 mM, pH 10.5), phosphate buffer (0.1 M, pH 7 and 8), and citric acid buffers (10 mM, pH 3, 4, 5, and 6), individually, the UV–vis spectra of these suspensions were measured after 24 h to evaluate stability. One can see from Fig. 4 that the AuNPs are stable under different conditions without precipitation, which can be used to immobilize biomolecules on the surfaces of AuNPs in all of these media.

Size changes of AuNPs with copolymer shells in different pH buffers

It has been reported that a combination of PEO and PVP can produce a pH-sensitive hydrogel with different properties [61]. Recently, multi-responsive amphiphilic AuNPs protected by grafting poly(ether amine) have been prepared by a one-pot photochemical synthesis in the presence of thiograft poly(ether amine) [10]. To demonstrate the pH sensitivity, AuNPs were transferred to water and dialyzed against commercially available buffers with an increase pH from 3 to 10.5, and then DLS measurements were carried out. It is found that the average diameter (D_h) of



Scheme 1 Possible reactions during the formation of gold nanoparticles

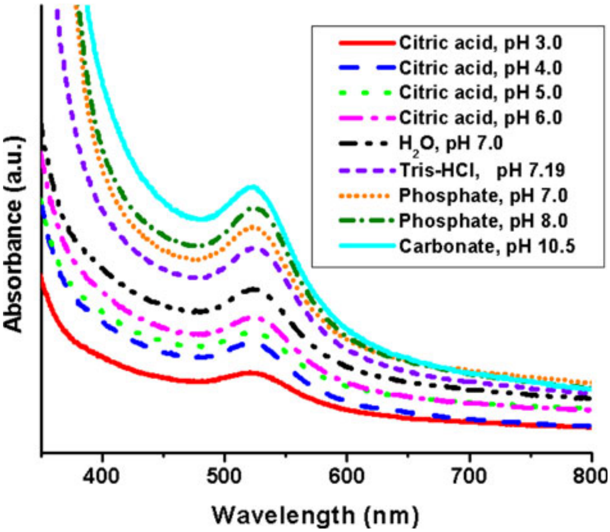


Fig. 4 UV–vis spectra of AuNPs with copolymer shells in water and pH buffers. Spectra were collected after 24 h in each medium

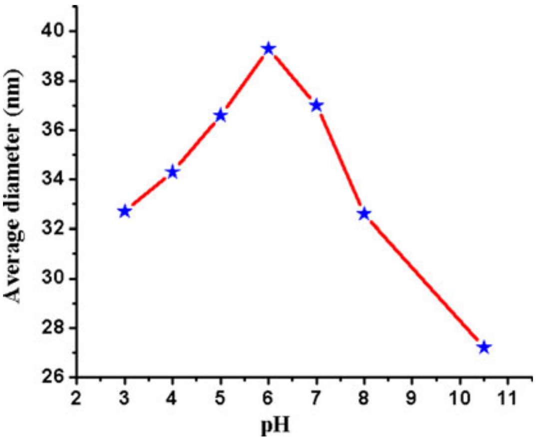


Fig. 5 The average diameters of AuNPs with PVP-*b*-PEO shells in different pH buffers measured by DLS at 25 °C

the AuNPs in water solution is much affected by the pH value (Fig. 5). In acidic solution, the values of D_h increase from 32.7 nm at pH 3 to 39.3 nm at pH 6. Obviously, the D_h reaches the maximum value at pH 6. However, in the basic or neutral solution, an obvious trend to reduce the D_h (from 39.3 to 27.2 nm) is observable with the increase of pH value from 6 to 10.5. Usually, the mean pK_a of the PVP blocks is in the range of 4–6 [62–64], depending on the structural parameters of the copolymer. The pH-dependent micellization of the PVP-*b*-PEO and the formation of interpolyelectrolyte complexes (IPEC) by mixing protonated PVP-*b*-PEO with poly(methacrylic acid)-*block*-poly(ethylene oxide)

(PMAA-*b*-PEO) were also discussed in detail [62–64]. The protonation of the PVP blocks leads to the expansion of PVP-*b*-PEO due to the intra- and intersegmental electrostatic repulsion. However, the decrease in D_h with the decrease of pH from 6 to 3. This behavior may be rationalized as follows: the protonation of the PVP blocks with decreasing pH may promote hydrogen bonding between the charged PVP and the PEO segments within the cross-linked shell, which results in the shrinkage of the shell of AuNPs [65, 66]. The increase in pH (>6) leads to deprotonation of the PVP units and hence to unfavorable interaction between the chains of PVP and water. The PVP blocks should prefer a collapsed conformation with the resulting exclusion of water. Due to the shell structure are crosslinked, the deprotonation degree of the PVP increases with pH. Therefore, the average size of AuNPs also decreases as the pH increases from 6 to 10.5.

Reversibility study of AuNPs response to solution pH changes

For applications, it is also important to investigate the pH-dependent optical response of the AuNPs. We investigated the optical response of the AuNPs with PVP-*b*-PEO shells to repeated changes of the solution pH. In this case, the pH was adjusted by solutions of 1.0 M HCl and 1.0 M NaOH. It was observed that the AuNPs in water show distinct absorption maxima (λ_{max}) in the UV–vis spectra, while the pH of the sample was repeatedly cycled between 5.9 and 10.5 by addition of HCl and NaOH solutions (Fig. 6). At pH 5.9, the λ_{max} of the AuNPs was 529 nm, and at pH 10.5, the maximum shifted to 518 nm. During the cycling process, a gradual decrease of the λ_{max} at pH 5.9 was observed, which could be due to the change of the ionic strength of the solution [67].

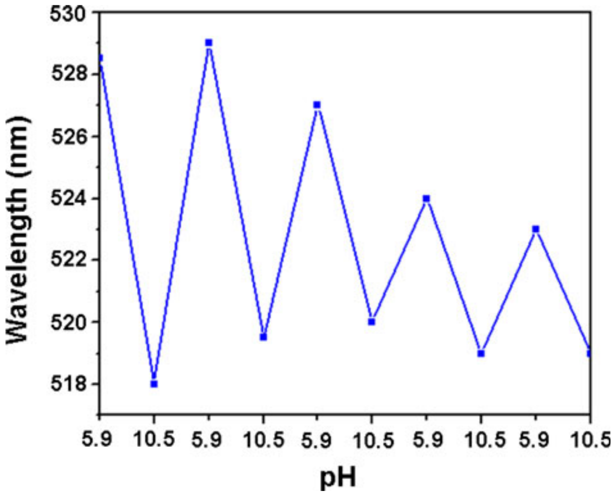


Fig. 6 Optical response of AuNPs as the solution pH was cycled. The pH was adjusted by 1.0 M HCl and 1.0 M NaOH solutions

Conclusions

An effective strategy for the preparation of pH-responsive AuNPs with PVP-*b*-PEO shells by UV irradiation of the solution of PVP-*b*-PEO/$HAuCl_4$ complexes is reported. The resultant AuNPs with PVP-*b*-PEO shells are well-dispersed and stable for a long time in organic solvents and various biochemical buffers. It is also found the average hydrodynamic diameter (D_h) of the AuNPs in water is much affected by the pH value. By monitoring optical changes of the AuNPs, the AuNPs were able to undergo five reversible cycles.

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