

Thermosensitive Au-PNIPA yolk-shell particles as “nanoreactors” with tunable optical properties

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Abstract We demonstrate that Au-silica-poly(*N*-isopropylacrylamide) (PNIPA) trilayer composite particles with controllable thickness of PNIPA out-layer can be developed via free radical polymerization using Au-silica core-shell particles as seed. The presence of Au-silica particles does not influence of thermosensitivity of PNIPA shell, which exhibits a similar swelling behavior as pure PNIPA microgels. The etching of silica midlayer by NaOH treatment leads to Au-PNIPA particles with yolk-shell structure. The obtained yolk-shell particles can work as “nanoreactors” for the further growth of Au core within the PNIPA shell via seeded growth approach, which is followed with interesting optical properties. In addition, the optical properties of the Au cores can be modulated by the volume transition of the PNIPA shell.

Keywords Thermosensitive · Microgels · Yolk-shell · Metal nanoparticles · Optical properties

Introduction

Metallic nanoparticles exhibit properties differing markedly from the properties of the bulk metal [1], which have been widely applied in catalysis [2, 3], sensors [4], optics [5, 6], etc. For example, gold and silver nanoparticles have shown unique optical properties, such as plasmonic optical response, from which various applications have been explored [5, 7, 8]. One of the major challenges for the preparation and application of metallic nanoparticles is their chemical and structural stability as they are ease to form coagulation. In addition, a precise control over the size and shape of the metal nanoparticles with a low polydispersity is essential for their properties [9]. Thus, different stabilizer systems (such as micelles [10, 11], microgels [12, 13], dendrimers [14, 15], etc.) and nanostructures (such as core-shell [16], yolk-shell [17, 18], core-satellite [19], etc.) have been developed in the last few years, which could bind to or encapsulate the metal nanoclusters and prevent them from aggregation.

However, it is still a major task to develop carrier systems, which could tune the properties of the immobilized metal nanoparticles. The incorporation of metal nanoparticles within so-called “smart” microgels, which can react in a specific way to external stimuli, has become the current research focus [20–22]. Such hybrid particles will show a combination of “inorganic” and “organic” characteristics that the optical or catalytic features of the metal nanoparticles could be tuned by the stimuli-responsive behavior of the microgel carrier system [23]. Liz-Marzán et al. [24, 25] have developed core-shell colloidal system comprising Au nanoparticles coated with a thermosensitive poly(*N*-isopropylacrylamide) (PNIPA) microgel. In our previous study, thermosensitive polystyrene (PS)-PNIPA core-shell microgels were applied as the carrier system for the immobilization of different kinds of metal nanoparticles. It is found that the catalytic activity and optical properties of immobilized metal nanoparticles can be tuned by the swelling and shrinking of the thermosensitive microgels.

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Kawaguchi et al. [26, 27] have reported the color change of the thermosensitive hybrid core-shell particles with temperature, which is due to the change of interparticle distance of gold nanoparticles in the thermosensitive microgel with temperature. We have observed similar behavior for Au nanorods (NRs) embedded in core-shell microgels that a red shift of the longitudinal plasmon resonance of Au NRs can be clearly observed with increasing temperature, which can be correlated to the volume transition of the microgel carrier [21].

More recently, we have fabricated new functional hybrid particles with yolk-shell structure that contains a movable metallic gold core completely isolated by a stimuli-sensitive PNIPA shell [28]. We have demonstrated for the first time that such yolk-shell particles can work as active “nanoreactors”: the catalytic selectivity of Au nanoparticles can be tuned between hydrophilic and more hydrophobic molecules through the volume transition of PNIPA shell for the catalytic reduction of 4-nitrophenol and nitrobenzene in the presence of NaBH_4 . Comparison with other systems, yolk-shell type nanostructures that metal nanoparticles are encapsulated in hollow porous shells have shown excellent stability of the metallic nanoparticle during different applications [29]. In addition, for the PNIPA coated-Au particles, the surface of Au core should be either coated with a thin layer of polystyrene or modified with functional molecules for the coating of PNIPA shell. This will disturb the catalytic activity of Au cores. Thus, Au-PNIPA yolk-shell particles will be more suitable for the catalytic studies.

In the present study, we follow-up the above paths that Au-SiO₂-PNIPA trilayer composites with thermosensitive PNIPA shell have been first fabricated through free radical polymerization using Au-SiO₂ nanoparticles modified by 3-(trimethoxysilyl) propylmethacrylate (MPS) as the seeds. We can show that the thickness of PNIPA shell can be efficiently controlled by monomer concentration during synthesis. The SiO₂ layer can be further removed by NaOH treatment. Thus, Au-PNIPA yolk-shell particles are formed. In addition, the yolk-shell particles can work as “nanoreactors” that a second growth of the Au core in situ within the PNIPA shell can be realized by a seed-growth approach in the presence of cationic surfactant cetyltrimethylammonium bromide (CTAB) as shown in Fig. 1. The thermosensitivity as well as the optical properties of the obtained composite microgel particles have been investigated in detail. This demonstrates another possibility for the potential applications of yolk-shell particles as “nanoreactors”.

Experimental section

Chemicals

Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), sodium citrate tribasic dehydrate 99 %, (3-aminopropyl) trimethoxysilane

(APS), sodium silicate, MPS, tetraethyl orthosilicate 99 % (TEOS), poly (vinylpyrrolidone) ($M_w=10000$, PVP), potassium peroxodisulfate (KPS), *N*-isopropylacrylamide (NIPA), *N,N'*-methylene-bisacrylamide (BIS), CTAB 98 %, L-ascorbic acid (AA), ammonia solution 30 % and analytical grade ethanol were purchased from Aldrich and used as received. Milli-Q water with a resistivity higher than 18.2 M Ω was used in all preparations.

Synthesis of Au-SiO₂-MPS nanoparticles

Au-SiO₂ core-shell particles were prepared according to the techniques described by Liz-Marzán [30, 31]. In a typical run, 0.5 ml aqueous solution of APS (1 mM) is added to 50 ml of the gold sol (0.5 mM HAuCl_4) prepared by sodium citrate reduction method under vigorous magnetic stirring for 15 min. Two milliliters of freshly treated active silica (1.08 wt%) is then added to the surface modified gold sol under vigorous stirring. After 24 h, 200 ml ethanol is added into above gold solution to make 1:4 water/ethanol mixture, and then 0.15 ml TEOS and 1 ml ammonia is introduced into reaction. The reaction solution is allowed to stand for 48 h under mild magnetic stirring. The silica surface is finally functionalized by 1.6 ml of MPS. As-prepared surface-functionalized Au-SiO₂ nanoparticles were cleaned by centrifugation in ethanol several times and redispersed in 2.5 ml ethanol. The amount of MPS was calculated and adjusted to obtain a surface density of one molecule per 0.4 nm⁻² [32].

Synthesis of Au-SiO₂-PNIPA trilayer composite

In a typical run, 0.6 ml Au-SiO₂-MPS core-shell particles in ethanol solution (0.085 wt%) was dispersed in 12 ml PVP (2 wt%) aqueous solution under stirring. After 15 min, 0.293 g NIPA, and BIS (5 mol% of NIPA) mixture dissolved in 4 ml water was added inside. The solution was pre-heated to 35 °C under a nitrogen atmosphere and kept stirring for 15 min. After that, the temperature was raised to 70 °C and the polymerization started by the addition of initiator (10 mg KPS dissolved in 1 ml water). The red emulsion became turbid purple after 10 min and the polymerization lasted for 4 h at 70 °C. The purple and strongly turbid solution was then cooled to room temperature under stirring. The composite particles were then cleaned by centrifugation and redispersion in water several times.

Synthesis of Au-PNIPA yolk-shell particles

Au-PNIPA yolk-shell particle is prepared by a silica-etching procedure: 1 ml of NaOH (2 M) solution was added into 4 ml of Au-SiO₂-PNIPA suspension. The mixture was gently stirred at room temperature overnight and was cleaned by centrifugation.

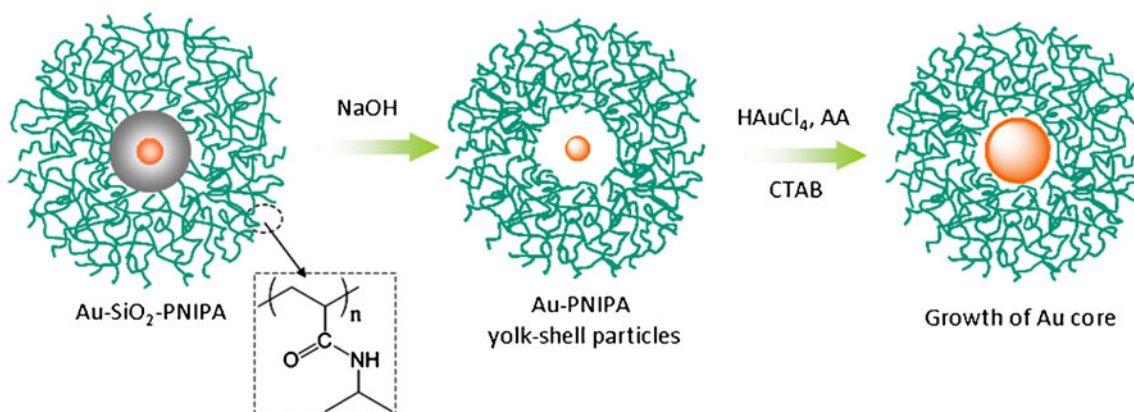


Fig. 1 Schematic illustration of the in situ growth of Au core using the Au-PNIPA yolk-shell particles as “nanoreactors” (details see text)

Growth of Au cores

The growth of Au cores was carried out following the method developed by Contreras-Cáceres et al. [33]. Briefly, to obtain Au (67 nm)-PNIPA particles, 2 ml of Au-PNIPA particles in 0.1 M CTAB solution ($[Au]=0.25$ mM) was added into 5 ml of 0.1 M CTAB solution containing 0.36 ml of 0.01 M HAuCl₄ and 0.072 ml of 0.1 M AA under magnetic stirring. After 2 h reaction in 28 °C, the suspension was cleaned through centrifugation. HAuCl₄ and AA amount was increased to 0.72 ml and 0.144 ml, respectively, in order to achieve Au (95 nm)-PNIPA particle.

Characterization

The UV–Vis spectra were measured with Lambda 650 spectrometer supplied by Perkin-Elmer with a temperature-controlled sample holder with an accuracy of ± 0.1 °C. Transmission electron microscopy (TEM) images were obtained with CM30 Philips microscope operating at an acceleration voltage of 300 kV. Cryogenic transmission electron microscopy was carried out as outlined in Ref [34]. The swelling behavior of thermosensitive microgel was determined by Malvern Zetasizer Nano ZS ZEN 3500 with a laser wavelength 532 nm at the angle of 173° and ran in the temperature range of 15 to 50 °C.

Results and discussion

Control of PNIPA shell thickness of the Au-SiO₂-PNIPA trilayer particles

Au-SiO₂-PNIPA trilayer composite particles are synthesized using Au-SiO₂ core-shell particles as seeds by the conventional radical polymerization using NIPA and BIS as monomers [28]. As shown in Fig. 2a, Au-silica core-shell particles with unique morphology have been

obtained, in which the Au core particles with diameter of 15 ± 3 nm are homogeneously coated with a silica shell of 26 ± 2 nm. Before the polymerization of PNIPA on the Au-SiO₂ particle surface, MPS molecule layer has been employed to functionalize the silica surface by providing C=C groups. The modification of the Au-SiO₂ surface via hydrolysis of MPS has been confirmed by FT-IR spectrum that the bands at 1,632 and 1,714 cm^{-1} can be clearly distinguished, which attribute to the stretching vibrations of the C=C and C=O groups of MPS component, respectively [35]. The silica-MPS shell has thickness of 26.5 ± 3 nm, which is slightly larger than that of silica shell without MPS.

MPS-modified Au-SiO₂ particles with vinyl groups on the surfaces are used as seeds in the emulsion polymerization for the formation of the cross-linked PNIPA polymer shell to afford monodisperse Au-SiO₂-PNIPA trilayer microspheres. PVP has been used as stabilizer during the polymerization in order to improve the stability of the MPS-modified Au-SiO₂ particles. The formation of PNIPA shell on the Au-SiO₂ particle surface has been first confirmed from TEM images as shown in Fig. 2. When 0.036 M of NIPA monomer is used, Au-SiO₂-PNIPA composite with PNIPA layer thickness of only 25 ± 3 nm is obtained. The composite dispersions are quite stable for a few weeks and no secondary PNIPA particle can be found in TEM images after washing procedure. Increase of NIPA monomer concentration for the polymerization leads to the increase of the thickness of PNIPA shell as seen from the TEM images of the particles. This has been also confirmed by DLS measurements that the hydrodynamic diameter of the microgel particles increases with the increase of the NIPA concentration as shown in Fig. 3. Increasing NIPA monomer amount to 0.144 M, PNIPA shell with thickness about 125 nm can be observed from the TEM image shown in Fig. 2e, which are homogeneously coated on the Au-SiO₂ surface.

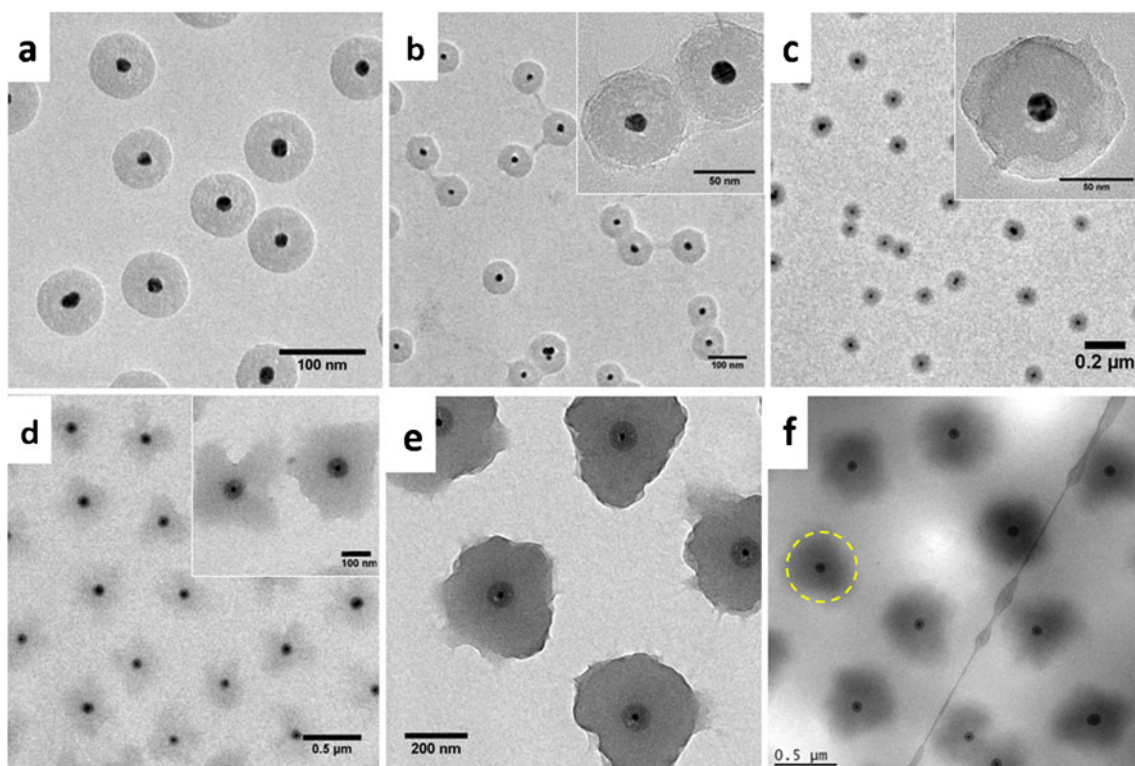


Fig. 2 TEM images of **a** Au-SiO₂ core-shell nanoparticles; Au-SiO₂-PNIPa trilayer composites synthesized with different NIPA monomer concentrations **b** 0.036 M, **c** 0.072 M, **d** 0.108 M, and **e** 0.144 M during polymerization; **f** cryo-TEM image of Au-SiO₂-PNIPa sample shown in **e**

Cryo-TEM image has been also taken to investigate the morphology of the composite particles in situ, that is, PNIPa shell is in its swollen state as shown in Fig. 2f. Here, a much thicker PNIPa shell of ca. 270 nm compared to the

shell thickness from TEM image has been determined, which agrees well with the thickness of the PNIPa shell determined by DLS at room temperature. As a reference, polymerization of NIPA has been also performed by using

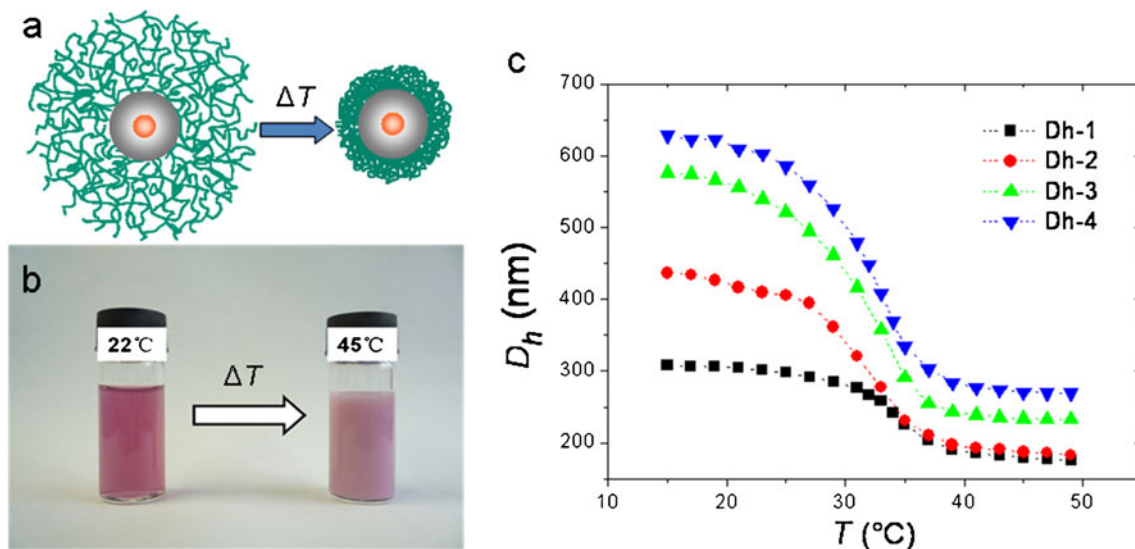


Fig. 3 **a** Scheme of phase transition and **b** photograph of Au-SiO₂-PNIPa composites from 22 to 45 °C for sample Dh-4. **c** Variation of the hydrodynamic diameters of the Au-SiO₂-PNIPa composite particles as a function of temperature. Samples Dh-1, Dh-2, Dh-3, and Dh-

4 are the microgel particles prepared with (black square) 0.036 M, (red circle) 0.072 M, (green triangle) 0.108 M, and (blue triangle) 0.144 M NIPA monomer, respectively

Au-SiO₂ particles without MPS-surface-modification as seeds, agglomeration is formed in this case and the system is unstable. This gives evidence that the vinyl group on the Au-SiO₂ particle surface is essential for the grafting of polymer onto silica.

The Au-SiO₂-PNIPA particles are thermosensitive inasmuch as the composites dispersion changed from purple at room temperature to strong turbid purple at 45 °C due to the increase in scattering with temperature. This change is clearly visible in Fig. 3b. The thermoresponsive properties of the microgel particles have been characterized in detail by DLS measurements. Figure 3c displays the variation of the hydrodynamic diameter of the Au-SiO₂-PNIPA particles when the temperature is varied from 15 to 50 °C. As expected there is a strong change in size induced by the change of the temperature. The well-defined volume transition temperature is found to be around 32 °C, which is similar to ordinary PNIPA microgels [36]. In addition, the transition is fully reversible under the heating–cooling circles. This indicates that the presence of Au-SiO₂ template does not significantly affect the swelling behavior of the PNIPA shell.

Fabrication of Au-PNIPA yolk-shell particles and growth of Au core

Previous studies indicate that the porosity of the PNIPA microgel shell offers the possibility to carry out selective chemical reaction on the encapsulated nanoparticles [21, 24, 28]. In the present study, the silica midlayer of the resultant Au-SiO₂-PNIPA composites can be selectively removed by etching with NaOH, which leads to the Au-PNIPA yolk-shell particles. As shown in Fig. 4a, Au-PNIPA composite particles with yolk-shell morphology have been formed. The PNIPA shell and movable Au core keep their original size and formation

before etching procedure (Fig. 2e). In addition, obtained Au-PNIPA yolk-shell particles can work efficiently as “nanoreactors” for the further growth of Au core. The movable Au core can be used as seeds for the second growth of Au nanoparticles in situ via ascorbic acid reduction of HAuCl₄ in the presence of CTAB. Using CTAB, it can efficiently avoid secondary nucleation in the solution and control the final size of Au nanoparticle. As reported by Liz-Marzán [24], complexation of tetrachloroauric acid with CTAB molecules leads to a change in the redox potential of Au(III) in such a way that the addition of ascorbic acid can only reduce Au(III) to Au(I) and not to Au⁰. However, addition of gold seeds favors the catalytic reduction of the gold salt complex by this mild reducing agent, so that it takes place selectively at the metal surface. TEM images shown in Fig. 4 reveal a noticeable increase in Au size, which varied from 67±5 nm (Fig. 4b) up to 95±6 nm (Fig. 4c) dependent on the reactant concentration (see experiment section). No secondary Au nanoparticles have been observed. As a consequence of the growth of Au core, the morphology of Au-PNIPA particles changes from yolk-shell type to core-shell type.

The optical properties of the Au-PNIPA composite particles after growth of Au core have been determined by UV–Vis spectroscopy. As shown in Fig. 5, with the increase of Au core from 15 to 67 nm, a red shift of surface plasmon absorption band from 529 to 547 nm can be clearly seen with band broadening. The absorption band shifts further to 573 nm when the Au core is increased to 95 nm. In addition, there is a continuous increase of the absorption intensity of the absorption band with the increase of Au core size. This finding agrees well with the results reported for the growth of Au colloids [30], which demonstrates that the presence of PNIPA shell does not disturb the growth of Au cores.

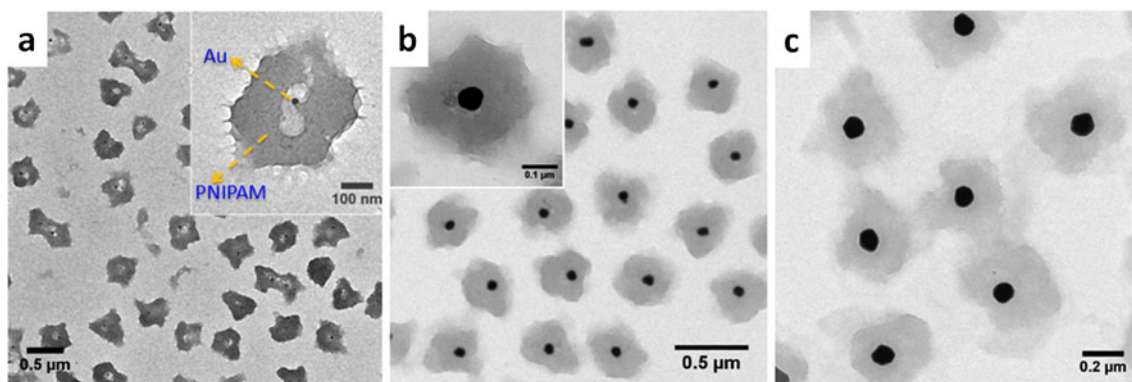


Fig. 4 a TEM image of Au (15 nm)-PNIPA yolk-shell particles. TEM images of b Au (67 nm)-PNIPA and c Au (96 nm)-PNIPA after further growth of 15 nm Au cores from PNIPA hollow microsphere

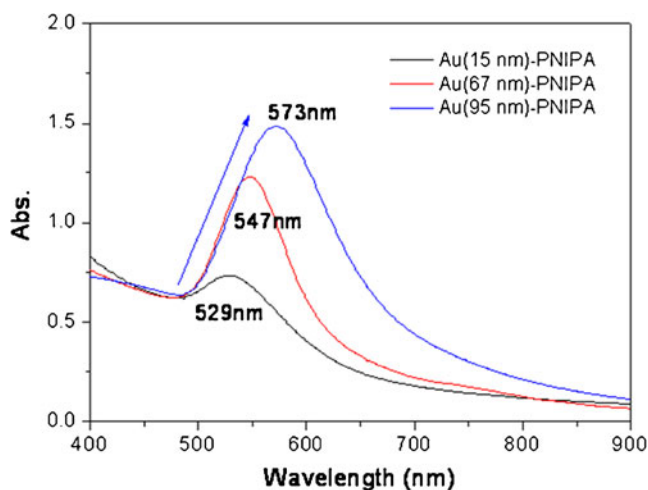


Fig. 5 UV-Vis spectra of Au-PNIPA yolk-shell particles after the further growth of Au cores

Thermoresponsibility of Au-PNIPA composite particles

The thermoresponsive properties of the Au-PNIPA yolk-shell particles after further growth of Au cores have been measured by DLS as a function of temperature as shown in Fig. 6a. Again, all the Au-PNIPA composite particles show typical lower critical solution temperature (LCST) behavior of the PNIPA networks with a volume transition temperature at around 32 °C. The hydrodynamic diameter of the Au-PNIPA composite particles increases slightly with the increase of Au core size, which is more obvious at temperatures above LCST.

It has been reported that the volume transition of the PNIPA shell affects the surface plasmon absorption behavior of metal nanoparticles, which may be traced back to the corresponding changes in the local refractive index [21, 24]. To observe optical properties of Au-PNIPA composite particles, UV-Vis measurements have been performed as a function of temperature. As shown in Fig. 6b, a red shift as large as 10 nm of surface plasmon absorption band can be clearly observed from the UV-Vis spectra for Au(95 nm)-PNIPA particles recorded between 15 °C (completely swollen state as determined by light scattering) and 50 °C (completely collapsed microgel). In addition, an increase in absorbance has been also shown. Both effects are likely caused by an increase in refractive index of the microgel during its collapse as well as an increase of the local refractive index around the Au core nanoparticles, which leads to a red shift and enhancement of the surface plasmon band [24]. This demonstrates that Au-PNIPA yolk-shell nanoparticles can act as an efficient, stable, thermoresponsive active “nanoreactors” for the in situ growth of Au cores that the optical properties of Au core can be modulated by the volume transition of PNIPA shell. This could create new

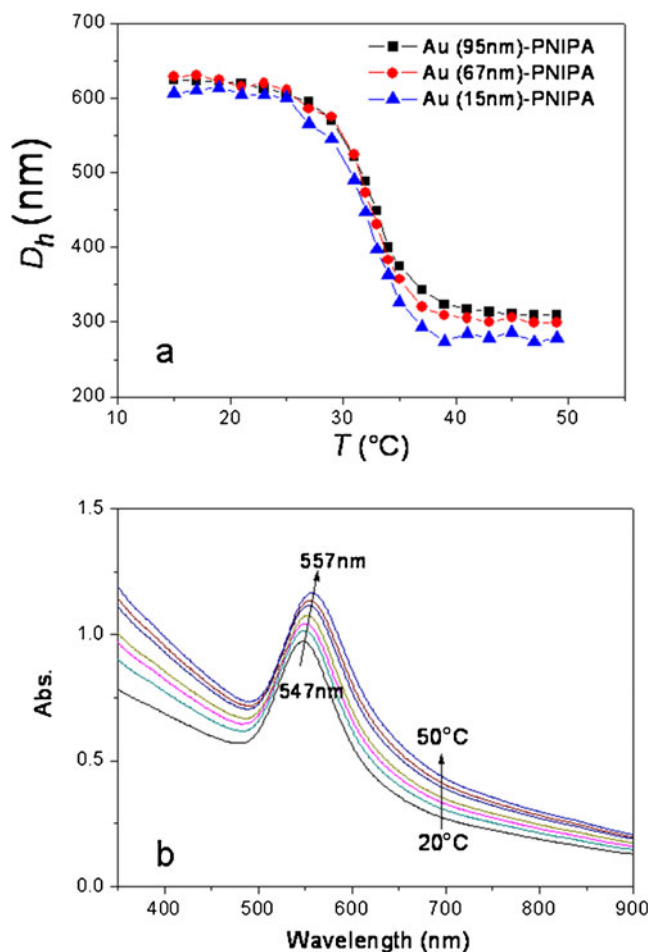


Fig. 6 a Hydrodynamic diameters of Au-PNIPA yolk-shell particles after further growth of Au cores measured at different temperatures. The dashed lines are to guide the eye. b UV-Vis spectra of Au(95 nm)-PNIPA composite particles measured as function of temperature

opportunities for development of novel stimuli-sensitive hybrid structures in nanotechnologies.

Conclusion

In summary, PNIPA shell with controllable thickness can be successfully deposited onto Au-silica core-shell particles via seeded emulsion polymerization. Etching of silica midlayer from the Au-silica-PNIPA composite particles leads to the Au-PNIPA yolk-shell particles. All the composite particles show similar swelling behavior as that of pure PNIPA microgels. The obtained yolk-shell particles work as “nanoreactors” that the Au core can be grown within the microgel leading to interesting optical property. In addition, the optical properties of the Au-PNIPA composite particles can be tuned by the thermosensitive PNIPA shell. This gives a promising possibility for the potential applications of yolk-shell particles as “nanoreactors”.

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