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Fabrication of Thermoresponsive Cross-Linked Poly(*N*-isopropylacrylamide) Nanocapsules and Silver Nanoparticle-Embedded Hybrid Capsules with Controlled Shell Thickness

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Supporting Information

ABSTRACT: We report on the fabrication of thermoresponsive cross-linked hollow poly(*N*isopropylacrylamide) (PNIPAM) nanocapsules and silver nanoparticle-embedded hybrid PNIPAM nanocapsules with controlled shell thickness via the combination of surfaceinitiated atom transfer radical polymerization (ATRP) and "click" cross-linking. Starting from initiator- functionalized silica nanoparticles, the surface-initiated ATRP of *N*-isopropylacrylamide (NIPAM) and 3-azidopropylacrylamide (AZPAM) afforded hybrid silica nanoparticles surface coated with P(NIPAM-*co*-AZPAM) brushes. Hybrid PNIPAM nanocapsules were then fabricated by the "click" cross-linking of PNIPAM shell layer with a trifunctional molecule, 1,1,1-tris(4-(2-propynyloxy)phenyl)ethane, followed by the subsequent removal of silica cores via HF etching. Shell cross-linked hybrid silica nanoparticles can further serve as



templates for the in situ preparation of silver nanoparticles within the cross-linked PNIPAM layer. After HF etching, silver nanoparticle-embedded hybrid PNIPAM nanocapsules were obtained. Due to the thermoresponsiveness of PNIPAM, cross-linked PNIPAM nanocapsules and silver nanoparticle-embedded hybrid PNIPAM nanocapsules exhibit thermo-induced collapse/swelling transitions. In the latter case, the spatial distribution of Ag nanoparticles within the hybrid PNIPAM nanocapsules can be facilely modulated by temperature variations, as revealed by the thermo-induced red shift of surface plasmon absorption band. Dynamic laser light scattering (LLS) measurements revealed that PNIPAM nanocapsules and Ag nanoparticle- embedded hybrid silica/ PNIPAM nanocapsules exhibit more prominent thermo-induced dimensional changes, as compared to shell cross-linked hybrid silica/ PNIPAM nanocapsules loaded with or without Ag nanoparticles, respectively. Due to that the surface-initiated ATRP can be conducted in a controlled manner, the current strategy employed for the fabrication of structurally stable cross-linked PNIPAM nanocapsules and Ag nanoparticle-embedded hybrid PNIPAM nanocapsules and Ag nanoparticle-embedded hybrid PNIPAM nanocapsules and hybrid rows-linked PNIPAM nanocapsules and Ag nanoparticle-embedded hybrid PNIPAM nanocapsules and hybrid rows-linked PNIPAM nanocapsules and Ag nanoparticle-embedded hybrid PNIPAM nanocapsules and Ag nanoparticle-embedded hybrid PNIPAM nanocapsules can be further applied to the preparation of other functional hollow hybrid nanostructures with controlled dimensions.

KEYWORDS: thermoresponsive nanocapsules, hybrid capsules, silica nanoparticles, spatial distribution, silver nanoparticles, poly(*N*-isopropylacrylamide), surface-initiated ATRP

■ INTRODUCTION

Hollow polymeric nanocapsules have attracted great interest in recent years due to their broad applications in controlledrelease carriers, catalysis, nanoreactors, and encapsulation of guest molecules.^{1,2} Polymeric nanocapsules have been typically fabricated via the self- assembly of block copolymers,^{3–5} polymerization within lipid vesicles,⁶ emulsion polymerization,^{7–14} and the sacrificial core-template approach.^{15–32} The latter can provide extra advantages such as ease of fabrication and tunable sizes of the hollow void. The sacrificial core-template approach typically involves the covalent or noncovalent attachment of polymer shells onto the surface of inorganic or organic core templates, followed by the subsequent core etching step.

Core templates can be coated with polymer shells via layer-bylayer (LBL) adsorption^{15,16,18,23,26} or surface polymerization techniques. In the latter case, precipitation polymerization in the presence of core templates were commonly employed for the preparation of hollow polymeric nanocapsules.^{19–21,24,27,29,33–35} However, the accurate control over shell thickness of hollow nanostructures is difficult as the free radical polymerization process can not be solely restricted at the surface of core templates. Developments in the field of controlled radical polymerization (CRP) in the past 20 years have rendered surface-initiated CRP as an indispensible approach for the fabrication of hybrid nanoparticles coated with polymer brushes of uniform thickness and predetermined chemical structures,^{36–39} which in turn has allowed for the facile preparation of uniform polymeric nanocapsules with controlled shell thickness. In a typical

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example, Walt et al.⁴⁰ prepared hollow poly(benzyl methacrylate) (PBzMA) nanocapsules via surface-initiated atom transfer radical polymerization (ATRP) of BzMA from silica nanoparticles and the subsequent removal of silica cores.

To further improve the structural stability of hollow polymeric nanocapsules, the covalent cross-linking approach has been introduced in combination with the surface-initiated CRP from core templates.^{41–47} A three-step approach has been typically employed. Relatively uniform polymer layers bearing reactive functionalities were grafted at the surface of nanoparticles via surface-initiated CRP at first, the polymer layer was then covalently cross-linked; in the final step, the core templates were removed via physical or chemical treatments to afford hollow polymeric nanocapsules. In this context, Hawker et al.⁴¹ synthesized hybrid silica nanoparticles grafted with poly(styrene-covinylbenzocyclobutene) or poly(styrene-co-maleic anhydride) brushes via surface-initiated nitroxide-mediated radical polymerization (NMP), and cross-linking of the polymer shell was achieved either thermally (coupling of benzocyclobutene moieties) or chemically via the addition of diamines; subsequently, the core etching step afforded stable cross-linked hollow polystyrene (PS) nanocapsules. Wang et al.⁴³ synthesized hybrid gold nanoparticles grafted with water-soluble copolymers containing 2-(dimethylamino)ethyl methacrylate (DMA) moieties via surface-initiated ATRP; cross- linked hollow nanocapsules were then obtained upon addition of 1,2-bis(2-iodoethoxy)ethane and the subsequent etching of Au cores. Later on, Kang et al.42 synthesized hybrid silica nanoparticles coated with polystyrene-*b*-poly(methyl methacrylate), PS-*b*-PMMA, brushes via surface-initiated ATRP; the subsequent UV irradiation led to the cross-linking of inner PS layer and the etching of PMMA outer layer; finally, cross-linked PS nanocapsules were obtained by HF etching of silica cores. Recently, Fukuda et al.⁴⁴ fabricated hybrid silica nanoparticles surface grafted with diblock copolymer brushes with the inner layer being poly(3-ethyl-3-(methacryloyloxy)methyloxetane) sequences, which can be cross-linked via the subsequent cationic ring-opening reaction of oxetane moieties.

It is worthy of noting that most of the above examples of crosslinked polymeric nanocapsules fabricated via surface-initiated CRP, cross-linking, and core etching steps are hydrophobic and poorly dispersible in aqueous media. Recently, waterdispersible cross-linked hollow polymeric nanocapsules responsive to external stimuli such as pH,^{6,27,29,43,48–50} temperature,^{19,21,24,25,27,33–35,48,51–53} and ionic strengths^{6,48} have drawn considerable attention due to the tunable permeability of polymer shells, which are quite advantageous for the controlled release of encapsulated guest molecules.⁵⁴ The preparation of cross-linked hollow poly(*N*-isopropylacrylamide) (PNIPAM) nanocapsules has been extensively explored. PNIPAM has been well-known as a thermoresponsive polymer, exhibiting a lower critical solution temperature (LCST) at ~32 °C in aqueous media.⁵⁵

Previously, cross-linked PNIPAM nanocapsules have been prepared by direct inverse miniemulsion polymerization of NIPAM in the presence of N,N'-methylenebisacrylamide (BIS),⁵² precipitation polymerization of NIPAM and BIS in the presence of core templates followed by core etching,^{19,24} and the fabrication of noncovalently connected core—shell nanoparticles followed by shell cross-linking and core etching.²¹ In addition, two-stage free radical precipitation polymerization was also developed to prepare cross-linked hollow PNIPAM nanocapsules by Lyon et al.,³³ and they fabricated core—shell PNIPAM microgels with the core cross-linked by degradable cross-linker and the shell cross-linked with nondegradable cross-linker (BIS); thus, the selective core degradation afforded cross-linked hollow PNIPAM nanocapsules. Later on, Wu et al.³⁴ proposed a one-pot synthetic strategy to prepare hollow PNI-PAM nanocapsules. The initially formed nuclei during the precipitation polymerization of NIPAM were directly used as core templates for the subsequent polymerization of NIPAM and BIS in the nucleus-growing stage. The noncross-linked PNIPAM core then spontaneously penetrated through the cross-linked shell to form hollow PNIPAM nanocapsules at temperatures below the LCST.

It should be noted that thermoresponsive cross-linked PNI-PAM nanocapsules have not, to the best of our knowledge, been fabricated by integrating surface-initiated CRP from nanoparticle core templates with the subsequent cross-linking and core etching, which should provide additional advantages such as controlled shell thickness, tunable cross-linking density, and thermo-modulated shell permeability. Moreover, metal nanoparticle/polymer hybrid nanomaterials combining the excellent optical and electronic properties of inorganic nanoparticles and the responsiveness of polymer matrix have recently emerged to be a hot research topic. In the context of PNIPAM matrix, hybrid nanoparticles with PNIPAM shells, PNIPAM microgels, and PNIPAM-based unimolecular micelles have been employed as templates for the immobilization of Ag and Au nanoparticles.⁵⁶⁻⁶² PNIPAM can serve as the immobilizing matrix of inorganic nanoparticles to prevent their aggregation, furthermore, its responsiveness allows for thermo-modulated catalytic and optical properties. For example, Ballauff et al.^{58,59} previously prepared hybrid PS/PNIPAM core-shell particles embedded with Ag nanoparticles in the PNIPAM shell. By taking advantage of the thermal volume phase transition (VPT) of PNIPAM shells, the spatial distribution of Ag nanoparticles and the catalytic efficiency can be tuned via temperature variations.

As compared to PNIPAM-based core—shell nanoparticle templates, hollow PNIPAM nanocapsules can swell or shrink to a larger extent. Just recently, Xie et al.³⁵ fabricated hollow PNIPAM nanocapsules via two-step precipitation polymerization at first and then employed them as templates for the coordination and in situ reduction of Ag^+ ions. However, there exist free Ag nanoparticles in the hollow void. The free radical nature involved in the precipitation polymerization process for the preparation of hollow PNIPAM nanocapsules intrinsically leads to hybrid nanocapsules of less well-defined microstructures, and uncontrolled and nonuniform shell thickness.

In recent years, the combination of click chemistry and surface-initiated CRP provides a versatile strategy to prepare well-defined functional hybrid nanoparticles.⁶³⁻⁶⁷ Click chemistry possesses advantages such as high specificity, facile purification, and quantitative yield in both protic and aprotic media. In this context, Ranjan and Brittain et al.^{63,64,66} fabricated hybrid silica nanoparticles densely grafted with polymer brushes by either "grafting to" or "grafting from" approaches involving the "click" technique. In a recent work by Li and Benicewicz,⁶⁵ a functional monomer with azido moiety, 6-azidohexyl methacrylate (AHMA), was polymerized at the surface of silica nanoparticles via CRP. Hybrid functional silica nanoparticles were then prepared by "click" modification with alkynyl-containing molecules. It should be noted that "click" chemistry has not been involved in the fabrication of cross-linked PNIPAM (hybrid) nanocapsules.

Scheme 1. Schematic Illustration of the Preparation of Hollow Poly(*N*-Isopropylacrylamide) (PNIPAM) Nanocapsules via the Combination of Surface-Initiated Atom Transfer Radical Polymerization (ATRP) and "Click" Cross-Linking, Followed by the Removal of SiO₂ Cores by HF Etching; The Obtained Hollow PNIPAM Nanospheres Exhibit Reversible Thermosensitive Swelling/Collapse Transitions



Scheme 2. Schematic Illustration of the Preparation of Silver Nanoparticle-Embedded Thermoresponsive Hybrid Nanocapsules; The Spatial Distribution of Silver Nanoparticles within Hybrid Nanocapsules Is Thermo-Tunable Due to the Reversible Swelling/ Collapse Transitions



In the present work, we fabricated thermoresponsive crosslinked hollow PNIPAM nanocapsules and silver nanoparticleembedded hybrid PNIPAM nanocapsules with controlled shell thickness via the combination of surface-initiated ATRP and "click" cross-linking (Schemes 1 and 2). Starting from initiatorfunctionalized silica nanoparticles, the surface-initiated ATRP of *N*-isopropylacrylamide (NIPAM) and 3-azidopropylacrylamide (AzPAM) afforded hybrid silica nanoparticles surface coated with P(NIPAM-*co*-AzPAM) brushes. Hybrid PNIPAM nanocapsules were then fabricated by the "click" cross-linking of PNIPAM shell layer with a trifunctional molecule, 1,1,1-tris-(4-(2-propynyloxy)phenyl)ethane, followed by the subsequent removal of silica cores via HF etching. Shell cross-linked hybrid silica nanoparticles can further serve as templates for the in situ preparation of silver nanoparticles within the cross-linked PNIPAM layer. After HF etching, hybrid PNIPAM nanocapsules with silver nanoparticles selectively embedded within the polymer shell were obtained. Due to the thermoresponsiveness of PNIPAM, cross-linked PNIPAM nanocapsules and silver nanoparticle-embedded hybrid PNIPAM nanocapsules exhibit thermo-induced collapse/swelling transitions. In the latter case, the spatial distribution of Ag nanoparticles within hybrid PNI-PAM nanocapsules can be facilely modulated by temperature variations.

EXPERIMENTAL SECTION

Materials. N-Isopropylacrylamide (NIPAM, 97%, Tokyo Kasei Kagyo Co.) was purified by recrystallization from the mixture of benzene and N-hexane (1/3, v/v). CuCl (99.999%), CuCl₂ (99%), CuBr

(99.999%), and N,N,N',N''-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich and used without further purification. Tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES) were purchased from Silicone Materials Co. (Wuhan Univ.) and distilled under reduced pressure just prior to use. Tris(2-(dimethylamino)ethyl)amine (Me₆TREN),³⁶ 1,1,1-tris(4-(2-propynyloxy)phenyl)ethane,⁶⁸ 3-azidopropylacrylamide (AzPAM),⁶⁹ and 2-bromoisobutyrate functionalized silica nanoparticles^{70,71} were synthesized according to previous literature reports. All other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

Sample Preparation. General approaches employed for preparation of hollow PNIPAM nanocapsules and silver nanoparticle-embedded hybrid PNIPAM nanocapsules were shown in Schemes 1 and 2, respectively.

Surface-Initiated ATRP of NIPAM and AzPAM from Initiator-Functionalized Silica Nanoparticles. Into a Schlenk flask equipped with a magnetic stirring bar, 2-bromoisobutyrate- functionalized silica nanoparticles (300 mg, 0.045 mmol initiator), Me₆TREN (40 mg, 0.17 mmol), CuCl₂ (2 mg, 0.015 mmol), NIPAM (4 g, 35.3 mmol), AzPAM (0.27 g, 1.75 mmol), and 2-propanol (4 mL) were charged. After the ultrasonic dispersion procedure, the mixture was degassed by one freeze-pump-thaw cycle. In the frozen state, CuCl (15 mg, 0.15 mmol) was added under the protection of N2 flow. The flask was subjected to two additional freeze-pump-thaw cycles and then placed in an oil bath thermostatted at 25 °C. In order to control the degree of polymerization (DP) of grafted P(NIPAM-co-AzPAM) chains at the surface of silica nanoparticles, the polymerization was conducted for different time periods (1, 2, 3, and 4 h) to achieve varying monomer conversions. After the desired polymerization time, the reaction flask was opened, exposed to air, and diluted with 2-propanol. Hybrid nanoparticles were isolated via centrifugation at \sim 15 000 rpm for 1 h and the sediments were then washed with ethanol. The above centrifugation-washing cycle was repeated for three times. The obtained hybrid silica nanoparticles coated with P(NIPAM-co-AzPAM) brushes were dried in a vacuum oven overnight at room temperature. A portion of obtained hybrid silica nanoparticles were dispersed in THF via ultrasonication. Surface grafted P(NIPAM-co-AzPAM) chains were then cleaved from silica cores via etching with hydrofluoric acid (HF, 47 wt %) for GPC measurement (Caution! HF is extremely corrosive, and all operations with aqueous HF should be conducted with suitable personal protective equipment).

Synthesis of Shell Cross-linked Hybrid Silica Nanoparticles and Hollow PNIPAM Nanocapsules (Scheme 1). Hybrid silica nanoparticles coated with P(NIPAM-co-AzPAM) brushes (4 h polymerization time as described above, 80 mg), 1,1,1-tris-(4-(2- propynyloxy)phenyl) ethane (2.5 mg, 0.006 mmol), PMDETA (10 mg, 0.058 mmol), and DMF (20 mL) were added into a Schlenk flask equipped with a magnetic stirring bar. After the ultrasonic dispersion procedure, the mixture was degassed by one freeze- pump-thaw cycle. In the frozen state, CuBr (9 mg, 0.063 mmol) was added under the protection of N_2 flow. The flask was then subjected to one additional freeze-pump-thaw cycle and then immersed into oil bath thermostatted at 80 °C. The mixture was stirred for 6 h. Nanoparticles were isolated via centrifugation at \sim 15 000 rpm for 1 h, the sediments were redispersed in ethanol, and subjected to further centrifugation. This purification cycle was repeated for three times. The obtained shell cross-linked hybrid silica nanoparticles were dried in a vacuum oven overnight at room temperature.

In a typical run for the preparation of hollow PNIPAM nanocapsules, shell cross-linked silica nanoparticles (10 mg) were dispersed in water (5 mL) by ultrasonication and hydrofluoric acid (47 wt %, 200 μ L) was added. After stirring for 2 h, the dispersion containing hollow PNIPAM nanocapsules was purified via dialysis against deionized water for 24 h at room temperature by using a dialysis membrane with a molecular weight cutoff of 7.0 kDa. The external solution was refreshed every 6 h during this period.

Fabrication of Silver Nanoparticle-Embedded Shell Cross-Linked Hybrid Silica Nanoparticles and Hybrid PNIPAM Nanocapsules (Scheme 2). Shell cross-linked silica nanoparticles (10 mg) obtained in the previous step were dispersed in deionized water (8 mL), 0.048 M AgNO₃ ($250 \,\mu$ L: high loading content; $32 \,\mu$ L: low loading content) was then added. After gently stirring for 1 h in the dark at 25 °C, the dispersion was subjected to brief dialysis against deionized water for 30 min. Freshly prepared aqueous solution of NaBH₄ (18 mg in 0.5 mL of water) was then quickly added, and the stirring was continued for 4 h. The dispersion of silver nanoparticle-embedded shell cross-linked hybrid silica nanoparticles was further purified via dialysis against deionized water for 24 h at room temperature by using a dialysis membrane with a molecular weight cutoff of 7.0 kDa. The external solution was refreshed every 6 h during this period.

In a typical run for the preparation of silver nanoparticle-embedded cross-linked hybrid PNIPAM nanocapsules, hydrofluoric acid (47 wt %, 100 μ L) was added into the dispersion of silver nanoparticle-embedded shell cross-linked hybrid silica nanoparticles (5 mL). After stirring for 2 h, the dispersion containing silver nanoparticle-embedded cross-linked hollow PNIPAM nanocapsules was purified via dialysis against deionized water for 24 h at room temperature. During this process, Fresh deionized water was replaced approximately every 6 h.

Characterization. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30 °C). It uses a series of three linear Styragel columns HT2, HT4, and HT5 at an oven temperature of 45 °C. The eluent was THF at a flow rate of 1.0 mL/min. A series of low polydispersity polystyrene standards were employed for the GPC calibration. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The spectra were collected at 64 scans with a spectral resolution of 4 cm^{-1} . Thermogravimetric analysis (TGA) was performed in air using a Perkin-Elmer Diamond TG/DTA at a heating rate of 10 °C/min. High-resolution transmission electron microscopy (HRTEM) observations were conducted on a JEOL 2010 electron microscope. The sample for HRTEM observations was prepared by placing 10 μ L solution on copper grids successively coated with thin films of Formvar and carbon and no staining step was conducted. The morphology of silver nanoparticle-embedded crosslinked hybrid silica nanoparticles and silver nanoparticle-embedded cross-linked hybrid PNIPAM nanocapsules were conducted on a JEOL JSM-6700 field-emission scanning electron microscope (FE-SEM). A commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multitau digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He–Ne laser ($\lambda_0 = 632$ nm) as the light source was employed for dynamic and static laser light scattering (LLS) measurements. In dynamic LLS, scattered light was collected at a fixed angle of 90° for duration of 15 min. Distribution averages and particle size distributions were computed using cumulants analysis and CONTIN routines. All data were averaged over three measurements. UV-vis absorption spectra of aqueous dispersion of silver composite hybrid silica nanoparticles and silver nanoparticle-embedded hybrid PNIPAM nanocapsules were acquired on a Unico UV/vis 2802PCS spectrophotometer with a thermostatically controlled couvette.

RESULTS AND DISCUSSION

Surface-Initiated ATRP of NIPAM and AzPAM from 2-Bromoisobutyrate-Functionalized Silica Nanoparticles. General strategies employed for the preparation of hybrid silica nanoparticles coated with thermoresponsive P(NIPAM-co-AzPAM) brushes are shown in Scheme 1. Previously, we have reported the preparation of hybrid silica nanoparticles surface grafted with PNIPAM brushes via surface-initiated ATRP and investigated the thermal phase transition behavior of PNIPAM homopolymer brushes at the surface of silica nanoparticles.⁷⁰ We also synthesized hybrid silica nanoparticles coated with two PNIPAM brush layers with the inner and out layer labeled with two types of fluorescent dyes, and the FRET process between them can be dually modulated by UV irradiation and the reversible thermoinduced collapse/swelling of PNIPAM brushes.⁷¹ In the current work, AzPAM monomer was introduced to copolymerize with NIPAM monomer, the polymer brush layer can then be subjected to further cross-linking reaction so that structurally stable cross-linked PNIPAM nanocapsules and silver nanoparticleembedded cross-linked hybrid PNIPAM capsules can be fabricated (Schemes 1 and 2).

2-Bromoisobutyrate-functionalized silica nanoparticles with an average radius of \sim 45 nm as determined by HRTEM (Figure 1a) were available from the previous work.⁷¹ Its typical synthesis was summarized as follows (Scheme 1). Bare silica NPs were prepared via the Stöber process,⁷² which were then modified with APTES to afford amine-functionalized silica nanoparticles; 2-bromoisobutyrate-functionalized silica NPs were prepared via the amidation reaction of amine-functionalized silica NPs with 2-bromoisobutyryl bromide. 2-Bromoisobutyrate-functionalized silica NPs were characterized by FT-IR analysis; the presence of amide moieties can be evidenced by the new appearance of a relatively weak amide II band (1540 cm⁻¹, N—H stretching) (Figure 2b), as compared to that of bare silica NPs (Figure 2a). Thermogravimetric analysis (TGA) reveals \sim 2.0 wt % difference in weight retentions at 650 °C between amine- and 2-bromoisobutyrate-functionalized silica NPs (Figure 3). If the mass retention of amine-functionalized silica NPs at 650 °C is used as the reference and the density of the silica NPs is assumed to be identical to that of bulk silica (2.07 g/cm^3) , the grafting density of ATRP initiators at the surface of silica NPs is roughly estimated to be ~ 0.31 nm²/ initiator. ATRP copolymerization of NIPAM and AzPAM (5 mol % relative to NIPAM) at the surface of initiator-functionalized silica NPs was conducted in 2-propanol at ambient temperature by using CuCl/CuCl₂ and Me₆TREN as the catalytic system. CuCl₂ (10 mol % relative to CuCl) was added in order to ensure an efficient exchange between the dormant and active species to control the surface-initiated ATRP. GPC analysis of P(NIPAMco-AzPAM) chains cleaved from silica cores (4 h polymerization time) via etching with hydrofluoric acid revealed an $M_{\rm p}$ of 46 000 and an M_w/M_n of 1.25 (Figure 4). The AzPAM content of P(NIPAM-co-AzPAM) copolymer was determined to be 4.8 mol % by ¹H NMR analysis. The relatively narrow polydispersity and almost symmetric GPC trace suggested that the surface-initiated ATRP can be conducted in a controlled manner. By adjusting the polymerization time and quenching the SI-ATRP at varying monomer conversions, four types of hybrid silica nanoparticles with the DP of grafted P(NIPAM-co-AzPAM) chains being 115, 221, 317, and 406 were fabricated. These results agree quite well with previous literature report.⁷⁰ As shown in Supporting Information Figure S1, the thickness of PNIPAM shell in hybrid silica nanoparticles was almost proportional to the DP of grafted P(NIPAM-co-AzPAM) chains. This is quite advantageous toward the fabrication of PNIPAM nanocapsules and silver nanoparticle-embedded hybrid capsules of controlled shell thickness after subjected to further cross-linking and core etching procedures (Schemes 1 and 2).

Figure 1b shows the HRTEM image of hybrid silica nanoparticles grafted with P(NIPAM-co-AzPAM) brushes, and it is



Figure 1. HRTEM images of (a) 2-bromoisobutyrate-functionalized silica nanoparticles, (b) hybrid silica nanoparticles coated with poly. (*N*-isopropylacrylamide-*co*-3-azidopropylacrylamide), P(NIPAM-*co*-AzPAM), brushes, (c) hybrid silica nanoparticles with the P(NIPAM-*co*-AzPAM) brush layer cross-linked via "click" reactions with 1,1, 1-tris(4-(2-propynyloxy)phenyl)ethane, and (d) hollow PNIPAM nano-capsules obtained by removing the silica cores of shell cross-linked hybrid silica nanoparticles via etching with HF.



Figure 2. Fourier transform infrared (FT-IR) spectra of (a) bare silica nanoparticles, (b) 2-bromoisobutyrate-functionalized silica nanoparticles, (c) hybrid silica nanoparticles coated with P(NIPAM-*co*-AzPMA) brushes, and (d) hybrid silica nanoparticles with the P(NIPAM -*co*-AzPAM) brush layer cross-linked via "click" reactions with 1,1,1-tris-(4-(2-propynyloxy)phenyl)ethane.

clearly evident that silica cores are surrounded by a polymer layer with a thickness of ca. 20 nm. Figure 2c shows the FT-IR spectrum of hybrid silica nanoparticles grafted with P(NIPAM*co*-AzPAM) brushes. The amide I band (1650 cm⁻¹, C=O stretching) and amide II band (1550 cm⁻¹, N—H stretching) can be clearly observed. The presence of two bands at 1367 and 1388 cm⁻¹ with almost equal intensity is associated with the deformation mode of two methyl groups on isopropyl of NIPAM.⁷³ In addition, the absorbance peak at ~2100 cm⁻¹ is characteristic of azido moiety of AzPAM. From the TGA results (Figure 3d), the weight retention at 650 °C obtained for P(NIPAM-*co*-AzPAM) grafted silica nanoparticles (4 h



Figure 3. Thermogravimetric analysis (TGA) of (a) bare silica nanoparticles, (b) amine- functionalized silica nanoparticles, (c) 2-bromoisobutyrate-functionalized silica nanoparticles, and (d) hybrid silica nanoparticles coated with P(NIPAM-*co*-AzPMA) brushes (4 h sample). TGA analysis was performed in air at a heating rate of 10 °C/min.



Figure 4. GPC trace of P(NIPAM-co-AzPMA) brushes (4 h sample) cleaved from hybrid silica nanoparticles via HF etching.

polymerization time) is ~41.5%, thus, the weight fraction of P(NIPAM-*co*-AzPAM) is calculated to be ~52.3% when aminefunctionalized silica nanoparticles are used as the reference. The grafting density of P(NIPAM-*co*-AzPAM) chains at the surface of silica NPs is estimated to be 1.9 nm²/chain by combining the TGA data and the molecular weight of grafted polymer chains (Figure 4). As the grafting density of ATRP initiators at the surface of silica nanoparticles is ~0.31 nm²/initiator, the initiating efficiency can be roughly estimated to be ~16%.

Synthesis of Shell Cross-Linked Hybrid Silica Nanoparticles and Cross-Linked Hollow PNIPAM Nanocapsules. Hybrid silica nanoparticles grafted with P(NIPAM-co-AzPAM) brushes were cross-linked via the "click" reaction of azido moieties within the polymer brush with trifunctional cross-linker, 1,1,1-tris(4-(2-propynyloxy)phenyl)ethane. Hollow PNIPAM nanocapsules were then obtained by removing silica cores via etching with HF (Scheme 1). It is worthy of noting shell-crosslinked hybrid silica nanoparticles are structurally similar to shell cross-linked micelles as originated by Wooley and co-workers. Figure 2d shows the FT-IR spectrum of shell cross-linked hybrid nanoparticles. The almost complete disappearance of characteristic azido absorbance peak at 2100 cm⁻¹ was observed after "click" cross-linking, confirming the high efficiency of "click" cross-linking reaction. HRTEM image of shell cross-linked hybrid silica nanoparticles shown in Figure 1c revealed that after shell cross-linking the thickness of polymer shell layer remained almost the same as that before cross-linking (Figure 1b). Moreover, the presence of isolated and relatively monodisperse spherical core-shell nanoparticles further suggested that the cross-linking reaction exclusively occurs within the polymer layer

and interparticle cross-linking reactions are negligible. After the etching of silica cores with HF, cross-linked PNIPAM nanocapsules with hollow microstructures were then obtained, as revealed by HRTEM analysis (Figure 1d). This confirms the successful crosslinking reaction which can maintain the structural integrity of hollow capsules; otherwise, after the etching step, we will not observe the presence of hollow nanocapsules. The overall dimension and shell thickness of cross-linked PNIPAM nanocapsules are relatively larger than those of shell cross-linked hybrid nanoparticles before the etching step (Figure 1c). This indicated that the etching step can lead to the expanding and swelling of the cross-linked polymer shells as the restriction of covalent linkage between the polymer layer and the solid silica nanoparticle core has been removed. Similar phenomena have been reported for hollow PNIPAM nanocapsules fabricated via the sacrificial core- template approach.^{19,21}

Synthesis of Silver Nanoparticle-Embedded Hybrid Silica Nanoparticles and Cross- Linked Hybrid PNIPAM Nanocapsules. Strategies employed for the in situ generation of silver nanoparticles within the cross-linked PNIPAM shell of hybrid silica nanoparticles and silver nanoparticle-embedded crosslinked PNIPAM hybrid capsules are shown in Scheme 2. Cross-linked PNIPAM nanocapsules were not chosen for the preparation of silver nanoparticle- embedded hybrid PNIPAM nanocapsules due to that uncontrolled generation of Ag nanoparticles within the hollow void can not be safely eliminated. In a typical procedure, aqueous dispersion of hybrid silica nanoparticles coated with cross-linked PNIPAM shell was treated with AgNO₃ solution. Uncomplexed Ag^+ ions were removed via brief dialysis against deionized water, which is an important process to prevent the formation of free silver nanoparticles in the bulk phase. The adsorbed Ag⁺ ions within the cross-linked polymer layer were then reduced into silver nanoparticles upon addition of aqueous NaBH₄ solution. According to previous works reported by Akashi, Ballauff, and Frey research groups, 56,59,75 Ag⁺ ions can preferentially coordinate with the nitrogen atom of amide moieties in PNIPAM. Frey et al.⁷⁵ reported that hydrated PNIPAM chains can act as the nucleating, capping, and stabilizing agent for the synthesis of silver nanoparticles in aqueous media, further implying the high affinity between PNIPAM segments and Ag nanoparticles. Moreover, the network nature of the outer cross-linked PNIPAM layer can further entrap and stabilize those in situ generated silver nanoparticles (Scheme 2). Figures 5a and 5c show HRTEM images of silver nanoparticleembedded cross-linked hybrid silica nanoparticles. We can see that silver nanoparticles with diameters in the range of 4–10 nm were selectively immobilized within the outer cross-linked polymer brush layer. Apparently, we can not discern the presence of free silver nanoparticles outside of hybrid silica particles by HRTEM, and this is in agreement with previous reports relevant to the fabrication of metal nanoparticle-embedded hybrid particles.^{58,59} To further exclude the presence of free silver nanoclusters (<1 nm) in the bulk phase, which is below the detection limit of HRTEM technique, the hybrid silica nanoparticle dispersion with silver nanoparticles embedded within the cross-linked PNIPAM layer was subjected centrifugation at $\sim 10\,000$ rpm for 30 min, the supernatant solution was partially condensed and subjected to fluorescence measurements. In the range of 400-800 nm, we can not observe any discernible fluorescence emission band which is characteristic of silver nanoclusters (<1 nm).⁷⁶ However, we still can not exclude the possibility that small silver nanoclusters might be present within the cross-linked PNIPAM brush layer of hybrid silica nanoparticles.



Figure 5. HRTEM (a-d) and SEM (e and f) images of (a, c, and e) shell cross-linked silica/PNIPAM hybrid nanoparticles with the cross-linked PNIPAM brush layer embedded with Ag nanoparticles (prepared at high AgNO₃ loading contents) and (b, d, and f) silver nanoparticle-embedded thermoresponsive PNIPAM hybrid nanocapsules obtained after HF etching of silica cores.

Apart from this, a closer examination and comparison of HRTEM images shown in Figures 1c and 5c for cross-linked hybrid silica nanoparticles before and after loading with silver nanoparticles revealed that for core—shell nanoparticles obtained after surface-initiated ATRP and shell cross-linking, there exists a outer diffusive polymer layer with relatively low chain density as compared to the polymer shell discerned by HRTEM (Figure 1b and c). The loading of silver nanoparticles clearly confirmed the presence of this outer diffusive layer (Figure 5a and c). This phenomenon can be all correlated with the previous results that PNIPAM-grafted hybrid silica nanoparticles possess double thermal phase transitions, with the one occurred at lower temperatures ascribed to the inner layer with high chain densities and the one at higher temperatures ascribed to the outer layer with relatively lower chain densities.⁷⁰

In the next step, silver nanoparticle-embedded cross-linked hybrid PNIPAM nanocapsules were prepared by etching the silica cores from silver nanoparticle-embedded hybrid silica nanoparticles (Scheme 2). Figure Sb and d show HRTEM images of silver nanoparticle-embedded hybrid PNIPAM nanocapsules, the size of which is much larger than that before etching, clearly suggesting the swelling of PNIPAM shells after removing the silica cores. A comparison of Figure 5a and c with Figure 5b and d indicated that the etching step has completely removed the silica cores. Though the presence of hollow voids with the nanostructures is not clearly evident from HRTEM images and we can only observe large hybrid PNIPAM particles homogeneously distributed with silver nanoparticles, SEM images shown in Figure 5e and f revealed the presence of cross-linked hollow hybrid PNIPAM nanocapsules after the etching step (Figure 5f). From Figure 5f, we can clearly observe the presence of hollow openings at the surface of nanocapsules, which is completely different from that before etching (Figure 5e).

The size and number density of silver nanoparticles within the cross-linked PNIPAM brush layer of hybrid silica nanoparticles and hybrid PNIPAM nanocapsules can be further tuned by varying the initial loading content of AgNO₃. Supporting Information Figure S2 shows HRTEM images of hybrid silica nanoparticles with the cross-linked PNIPAM layer embedded with silver nanoparticles and hybrid nanoparticle/PNIPAM nanocapsules prepared at a low AgNO₃ loading content. As compared to those prepared at high AgNO₃ loading content (\sim 4–10 nm; Figure 5), the diameters of silver nanoparticles at low AgNO₃ loading content are much smaller (\sim 2–5 nm) and their number density is also considerably lower. This might be ascribed to the fact that the low local concentration of Ag⁺ ions within PNIPAM shells can lead to slower nucleation and growth of silver nanoparticles.

In order to evaluate the average number density of silver nanoparticles within each hybrid PNIPAM capsule, TGA measurements were conducted for hybrid nanocapsules fabricated at high and low AgNO₃ loading contents (Supporting Information Figure S3). The weight retentions of hybrid nanocapsules were determined to be 20% and 1.6%, respectively. In combination with TGA results recorded for PNIPAM-grafted hybrid silica nanoparticles (Figure 3), and if we assume that silver nanoparticles take the same density as bulk silver (~10.53 g/cm³) and an average radius of ~3 nm and ~2 nm for silver nanoparticles prepared at high and low AgNO₃ loading contents, we can roughly estimate that each hybrid PNIPAM nanocapsule contains ~210 and ~46 silver nanoparticles, respectively.

Thermo-Induced Collapse/Swelling of Cross-Linked Hybrid Silica Nanoparticles and Hollow PNIPAM Capsules Loaded with or without Silver Nanoparticles. The average distance between neighboring grafted P(NIPAM-co-AzPAM) chains at the surface of silica NPs is estimated to be ${\sim}1.5~{
m nm}$ based on the average chain grafting density determined in the previous section. The degree of the polymerization (DP) of grafted P(NIPAM-co-AzPAM) chains (4 h polymerization time) is ca. 400. Preliminary experiments revealed that hydrodynamic dimensions of free P(NIPAM-co-AzPAM) chains with a DP of \sim 400 are much larger than the average distance (\sim 1.4 nm) between neighboring grafted P(NIPAM-co-AzPAM) chains, suggesting that the grafted P(NIPAM-co-AzPAM) layer falls into the polymer brush regime. Thus, grafted chains in the polymer brushes are crowded and forced to stretch away from the spherical silica substrate due to steric exclusion between neighboring chains. Dynamic LLS was then used to characterize the thermo-modulated changes in sizes and size distributions for cross-linked hybrid silica nanoparticles and hollow PNIPAM capsules loaded with or without silver nanoparticles in aqueous dispersion at varying temperatures.



Figure 6. Typical hydrodynamic radius distributions, $f(R_h)$, obtained at 20 and 35 °C for 1×10^{-6} g/L aqueous dispersions of (a) hybrid silica nanoparticles (4 h sample) coated with P(NIPAM- *co*-AzPMA) brushes, (b) hybrid silica nanoparticles with the P(NIPAM-*co*-AzPMA) brush layer cross-linked via "click" reactions with 1,1,1-tris(4-(2-propynyloxy)-phenyl)ethane, and (c) hollow PNIPAM nanocapsules obtained by removing silica cores via etching with HF.

Figure 6a shows typical hydrodynamic radius distributions, $f(R_{\rm h})$, of P(NIPAM-co- AzPAM) grafted hybrid silica nanoparticles at different temperatures. At 20 °C, R_h is in the range of 114–173 nm, with an average hydrodynamic radius, $\langle R_{\rm h} \rangle$, of 135 nm. Upon heating to 35 °C, R_h ranges from 89 to 145 nm, with an $\langle R_{\rm h} \rangle$ of \sim 108 nm. The polydispersity indexes of hybrid nanoparticles are 0.045 and 0.05 at 20 and 35 °C, respectively. The decrease of nanoparticle sizes at elevated temperature is ascribed to the collapse of PNIPAM brushes upon heating. Figure 6b shows $f(R_{\rm h})$ of shell cross-linked hybrid silica NPs at different temperatures. At 20 °C, Rh is in the range of 87-149 nm, with an $\langle R_h \rangle$ of 110 nm. Upon heating to 35 °C, $R_{\rm h}$ ranges from 70 to 101 nm, with $\langle R_{\rm h} \rangle$ of 85 nm. The polydispersity indexes of cross-linked hybrid nanoparticles are 0.06 and 0.04 at 20 and 35 °C, respectively. The size of the shell cross-linked hybrid silica nanoparticles at 20 °C is considerably smaller as compared to that before cross-linking, which should be due to the shrinking of polymer brushes caused by "click" crosslinking. The hydrodynamic radius of shell cross-linked hybrid silica nanoparticles also exhibit a decrease at 35 °C, which is similar to that displayed by uncross-linked hybrid silica nanoparticles. It can be calculated that the hydrodynamic volume of shell cross-linked hybrid silica nanoparticles shrunk \sim 2.2 times upon heating.

Figure 6c further shows $f(R_h)$ of hollow PNIPAM nanocapsules at different temperatures. At 20 °C, R_h is in the range of 124–197 nm, with an $\langle R_h \rangle$ of 157 nm, which is much larger than that of cross-linked hybrid nanoparticles before etching (135 nm). Upon heating to 35 °C, R_h ranges from 78 to 124 nm with an $\langle R_h \rangle$ of 94 nm. The polydispersity indexes are 0.055 and 0.05 at 20 and 35 °C, respectively. It is quite obvious that PNIPAM shell of the cross-linked hybrid silica nanoparticles swelled upon removing the silica core, which agrees quite well with the HRTEM results (Figure 1). We can calculate that hollow cross-linked PNIPAM nanocapsules shrunk ~4.6 times in hydrodynamic volumes upon heating from 20 to 35 °C. As compared to that of cross-linked hybrid silica nanoparticles



Figure 7. Typical hydrodynamic radius distributions, $f(R_h)$, obtained at 20 and 35 °C for 1×10^{-6} g/L aqueous dispersions of (a) shell crosslinked silica/PNIPAM hybrid nanoparticles with the cross-linked PNI-PAM brush layer embedded with Ag nanoparticles (prepared at high AgNO₃ loading contents), and (b) silver nanoparticle-embedded thermoresponsive PNIPAM hybrid nanocapsules obtained after HF etching of silica cores.

before etching (\sim 2.2 times), we can conclude that cross-linked PNIPAM nanocapsules display much larger extent of thermoinduced collapse/swelling.

Figure 7a shows $f(R_h)$ of silver nanoparticle-embedded shell cross-linked hybrid silica nanoparticles at different temperatures. At 20 °C, $R_{\rm h}$ is in the range of 96–164 nm with an $\langle R_{\rm h} \rangle$ of 115 nm. Upon heating to 35 °C, the $\langle R_h \rangle$ is \sim 92 nm. Compared to that before loading with silver nanoparticles, we can conclude that the thermosensitive properties of cross-linked PNIPAM layer were not hindered by the introduction of silver nanoparticles. Figure 7b shows $f(R_h)$ of silver nanoparticle-embedded hybrid PNIPAM nanocapsules at different temperatures. At 20 °C, R_h is in the range of 126–183 nm with an $\langle R_h \rangle$ of 150 nm. As compared to that before etching (Figure 7a), a large extent of swelling of the cross-linked hybrid polymer layer occurred due to the removal of silica cores. Upon heating, $\langle R_{\rm h} \rangle$ of silver nanoparticle- embedded cross-linked hollow PNIPAM capsules decreased to \sim 105 nm due to the collapse of PNIPAM network. Note that the thermo-induced collapse/ swelling transition was fully reversible for at least 6 heating-cooling cycles (Supporting Information Figure S4). It can be calculated that for silver nanoparticle-embedded shellcross-linked hybrid silica nanoparticles and hybrid PNIPAM nanocapsules, their hydrodynamic volumes in aqueous dispersion exhibit \sim 1.9 and 2.9 times of shrinking upon heating from 20 to 35 °C.

It is worthy of noting that for silver nanoparticle-loaded shellcross-linked hybrid silica nanoparticles and hybrid cross-linked PNIPAM nanocapsules, the thermo-induced collapse/swelling of polymer matrix layer can spontaneously modulate the spatial distribution of silver nanoparticles. UV—vis absorption spectrometry has been proved to be a convenient and powerful technique to monitor this via the shift of surface plasmon absorption band. Figures 8a and 8b show temperature-dependent UV—vis spectra of silver nanoparticle-loaded shell- crosslinked hybrid silica nanoparticles and hybrid cross-linked PNI-PAM nanocapsules (prepared at high AgNO₃ loading content), respectively. Both of them clearly exhibited a red-shift of surface plasmon absorption band upon heating from 20 to 37 °C.

Figure 9 shows temperature dependence of the wavelength of surface plasmon absorption peak maxima for silver nanoparticles embedded within the cross-linked PNIPAM shell layer of hybrid silica nanoparticles and hybrid PNIPAM nanocapsules. The surface plasmon peak maxima of silver nanoparticle-embedded shell-cross-linked hybrid silica nanoparticles gradually redshifted from 422 to 432 nm upon heating from 20 to 37 °C, whereas for silver nanoparticle-embedded hybrid PNIPAM nanocapsules, the peak maxima increased from 411 to 421 nm in the same temperature range. The red-shift of surface plasmon absorption band upon heating has been typically observed for silver nanoparticle/PNIPAM hybrid composites.35,58-60 When the temperature spans across the thermal phase temperatures of cross-linked PNIPAM matrix layers, the shrinkage of the polymer layer can greatly decrease the relative distance between neighboring sliver nanoparticles, leading to stronger interparticle coupling and the observed red shift of surface plasmon band.

Taking hybrid silica nanoparticles with silver nanoparticles embedded within the cross-linked PNIPAM layer as an example, we can more quantitatively calculate the changes of spatial distances between neighboring silver nanoparticles upon thermo-induced collapse of the outer PNIPAM brush layer by combining the above results of nanoparticle number density and volumetric changes of PNIPAM brush layers (Supporting Information Figure S3 and Figure 7). Upon heating from 20 to 35 °C, $\langle R_{\rm h} \rangle$ of silver nanoparticle-embedded shell cross-linked hybrid silica nanoparticles decreases from 115 to 92 nm (Figure 7a). As the silica core possesses a radius of 45 nm, we can estimate that the volume of hybrid cross-linked PNIPAM layer in a single hybrid nanoparticle decreased from 5.99 \times 10^6 nm³ to 2.88 \times 10⁶ nm³. From previous sections, we have determined that ~210 nanoparticles exist within each hybrid PNIPAM nanocapsule prepared at high AgNO₃ loading content. Assuming that silver nanoparticles are homogeneously distributed within the cross-linked brush layer, we can calculate that upon heating from 20 to 35 °C, the average distance between neighboring silver nanoparticles decreased from 31 to 23 nm for hybrid silica nanoparticles prepared at high AgNO₃ loading content. This qualitatively explains the thermo-induced red shift of surface plasmon absorption peak maxima.

From Figure 9, we can also observe that in the temperature range of 20-25 °C, the spatial distance between silver nanoparticles is quite large (~31 nm) when the PNIPAM layer is in the swollen state, which is unable to induce appreciable red shift of surface plasmon absorption peaks. Above 25 °C, the shrinkage of PNIPAM layer leads to much closer proximity between neighboring silver nanoparticles and the more prominent red shift of surface plasma peak maxima. It is worthy of noting that even at 37 °C, the calculated spatial distance (23 nm) between neighboring silver nanoparticle is still quite large to induce effective interparticle coupling as the distance between the periphery of two neighboring silver nanoparticles is as high as ~15 nm. However, we also need to consider the fact that silver



Figure 8. Temperature dependence of UV—vis spectra obtained for 5.0×10^{-5} g/L aqueous dispersions of (a) shell cross-linked silica/ PNIPAM hybrid nanoparticles with the cross-linked PNIPAM brush layer embedded with Ag nanoparticles (prepared at high AgNO₃ loading contents), and (b) silver nanoparticle-embedded thermoresponsive PNIPAM hybrid nanocapsules obtained after HF etching of silica cores.



Figure 9. Temperature dependence of the wavelength of surface plasmon absorption peak maxima recorded for 5.0×10^{-5} g/L aqueous dispersions of shell cross-linked silica/PNIPAM hybrid nanoparticles with the cross-linked PNIPAM brush layer embedded with Ag nanoparticles (\bullet) and silver nanoparticle-embedded thermoresponsive PNI-PAM hybrid nanocapsules obtained after HF etching of silica cores (\bigcirc).

nanoparticles are not homogeneously distributed within the cross-linked PNIPAM shell, the PNIPAM chain densities radially decrease from the core—shell interface outward to the outer periphery, leading to higher silver nanoparticle densities in the inner layer of cross-linked PNIPAM brush.

We can also note that in the temperature range of 20-37 °C, the wavelengths of surface plasmon peak maximum recorded for silver nanoparticle-embedded PNIPAM nanocapsules (411– 421 nm) are systematically lower than those of silver nanoparticle-embedded shell-cross-linked hybrid silica nanoparticles (422–432 nm), this is clearly correlated with the fact that in the former case, the spatial distance between silver nanoparticles is considerably larger due to that cross-linked hybrid PNIPAM nanocapsules possess larger dimensions, as evidenced from TEM and dynamic LLS results (Figures 5 and 7). Moreover, upon cooling from 37 to 20 °C for silver nanoparticle-embedded cross-linked PNIPAM nanocapsules, the surface plasmon peak maxima shift back to the original position at 20 °C (SI Figure S4). This type of thermo-induced shift and cooling-induced restoration of surface plasmon absorption band can be repeated for at least 6 cycles. The complete reversibility of the shift in surface plasmon band confirms that the thermo-induced collapse/swelling of hybrid PNIPAM nanocapsules is fully reversible, which is also consist with the DLS results (SI Figure S4).

CONCLUSION

Hollow PNIPAM nanocapsules and silver nanoparticle-embedded hybrid PNIPAM capsules with controllable shell thickness were prepared via the combination of surface-initiated atom transfer radical polymerization (ATRP) and "click" cross-linking. First, NIPAM and a functional monomer containing clickable moiety, 3-azidopropylacrylamide (AzPAM), were polymerized from the surface of silica NPs derivatized with ATRP initiators via surface-initiated ATRP; the polymer shells were then "click" cross-linked followed by the removal of silica cores to afford hollow PNIPAM nanocapsules. The shell cross-linked hybrid silica NPs can also serve as templates and nanoreactors for the in situ preparation of silver nanoparticles, and silver nanoparticleembedded hybrid PNIPAM nanocapsules were obtained after removing silica cores via etching. The obtained hollow PNIPAM nanocapsules as well as silver nanoparticle-embedded hybrid PNIPAM nanocapsules exhibited reversible thermo- induced swelling/collapse transitions and more prominent thermo-induced dimensional changes as compared to shell cross-linked hybrid silica/PNIPAM nanoparticles loaded without or with Ag nanoparticles. For silver nanoparticle-embedded hybrid PNI-PAM nanocapsules, the spatial distribution of Ag nanoparticles within cross-linked PNIPAM nanocapsules can accordingly be modulated via the reversible thermo-induced collapse/swelling of hybrid PNIPAM capsules. It can be envisioned that hollow PNIPAM nanocapsules and silver nanoparticle-embedded hybrid PNIPAM capsules could find potential applications in controlled-release nanocarriers, efficiency-tunable catalysis, and smart optic/electronic devices.

ASSOCIATED CONTENT

Supporting Information. The correlation between PNI-PAM shell thickness and the DP of grafted polymer chains, the changes of $\langle R_h \rangle$ and surface plasmon absorption peak maxima of silver nanoparticle-embedded hybrid PNIPAM nanocapsules upon heating—cooling cycles, additional HRTEM images, and TGA results. This material is available free of charge via the Internet at http://pubs.acs.org.

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