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Communications

Thermosensitive Gold Nanoparticles Based on Star-Shaped Poly(*N*-isopropylacrylamide) with a Cubic Silsesquioxane Core

Xiaojing Zhang*, Yuelei Hu, Ruixue Liu*, Jiashu Sun, and Shaoming Fang

College of Materials and Chemical Engineering,
Zhengzhou University of Light Industry, Henan Provincial
Key Laboratory of Surface and Interface Science,
Zhengzhou, P. R. China

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Introduction

In recent years, gold nanoparticles (AuNPs) have been extensively investigated due to their unique electronic, optical, catalytic and biocompatible properties, as well as their promising applications in biology and nanotechnology.[1-5] However, AuNPs are lack of sufficient stability and need to be protected by organic or inorganic stabilizer to avoid aggregation.[1,6-8] Using polymers as stabilizers can not only enhance stability, adjust the surface property of AuNPs, but also functionalize AuNPs *via* elaborate design of polymer. Recently, thermosensitive gold nanocomposites through the introduction of thermosensitive polymer such as poly(*N*-isopropylacrylamide) (PNIPAM) into AuNPs have attracted particular interest.[9-14] For example, Zhu *et al.*[9] polymerized a kind of thermosensitive gold nanoparticles by attaching a PNIPAM homopolymer terminated with dithioester groups *via* reversible addition fragmentation chain transfer (RAFT) on the surface of gold nanoparticles. The thermosensitive gold nanoparticles exhibited potential use for stimuli-responsive applications. Li *et al.*[10,11] synthesized Au@copolymer hybrids (the core-shell gold nanoparticles and copolymer of *N*-isopropylacrylamide (NIPAM) and *N,N'*-methylenebisacrylamide (MBA) hybrids) by atom transfer radical polymerization (ATRP) on the surface of gold nanoparticles. They used the free space of the copolymer-network scaffold anchored at the gold surface to trap and encapsulate smaller nanoparticles. Shen[12] *et al.* synthesized hyperbranched polyglycerols (HPGs) with NIPAM groups to coat water-soluble gold nanoparticles through noncovalent bonds, giving rise to nanoparticles with readily controllable lower critical solution temperatures (LCSTs) in a very broad temperature range (25-55 °C).

Polymeric oligomeric silsesquioxane (POSS) is an inorganic, cubic-shaped silica nanoparticle with a diagonal length of around 1.0 nm and a tunable overall molecular size depending on the size of the side groups,[15-17] having many potential applications in performance materials and biomedical fields.[18-21] POSS can be an ideal inorganic core to achieve well-defined hybrid star polymers due to its strong ability to be functionalized. Star polymer is an interesting class of macromolecules to its unique branched three-dimensional structures. They offer lower viscosity, higher chain end functionality and more interior space compared to linear polymers with similar molecular weight and composition.[22] The advantages of star polymers make them competitive as carriers of nanoparticles and drug molecules.[23] However, reports about thermo-sensitive star polymers with POSS core have been rare.[24,25] Yuan *et al.*[24] prepared a star-shaped hybrid P(2-(2-methoxyethoxy)ethylmethacrylate)-*co*-oligo(ethyleneglycol) methacrylate (P(MEO$_2$MA-*co*-OEGMA)) with polyhedral oligomeric silsesquioxane (POSS) core *via* ATRP. The obtained inorganic-organic hybrid polymers can self-assemble into micelles in aqueous solution with significant tunable temperature responsive property from 29.7 to 39.1 °C through altering the ratio of MEO$_2$MA and OEGMA in P(MEO$_2$MA-*co*-OEGMA) polymers. Bai *et al.*[25] synthesized temperature and pH dual-responsive dendritic POSS-poly(*N*-isopropylacrylamide)-poly(2-hydroxyethyl methacrylate) copolymers *via* atom transfer radical polymerization and click reactions, and investigated their structures. The cloud points (T_c) of dendritic POSS-PNIPAm-PHEMA copolymers are also affected by pH values with changes in hydrogen bonds interactions and solvation of PHEMA.

In the present study, we synthesized a novel star-shaped PNIPAM (POSS-*g*-PNIPAM) *via* ATRP with a POSS initiator, octa(2-bromobutylamidophenyl)silsesquioxane (OBAPS). Then, the thermo responsive star polymer POSS-*g*-PNIPAM was explored as the stabilizer of colloidal gold by direct mixing (Scheme I). The thermo-sensitivity, morphology and surface plasmon resonance (SPR) of the resulted hybrid Au nanoparticles (AuNPs) were investigated by transmission electron microscopy (TEM), UV-visible spectroscopy and dynamic laser scattering (DLS). The hybrid AuNPs show good stability and sensitivity to temperature with decreased lower critical solution temperature (LCST) compared to POSS-*g*-PNIPAM.

Results and Discussion

OBAPS initiator can be synthesized by the nitration, reduction and esterification reactions of octaphenyl silsesquioxane

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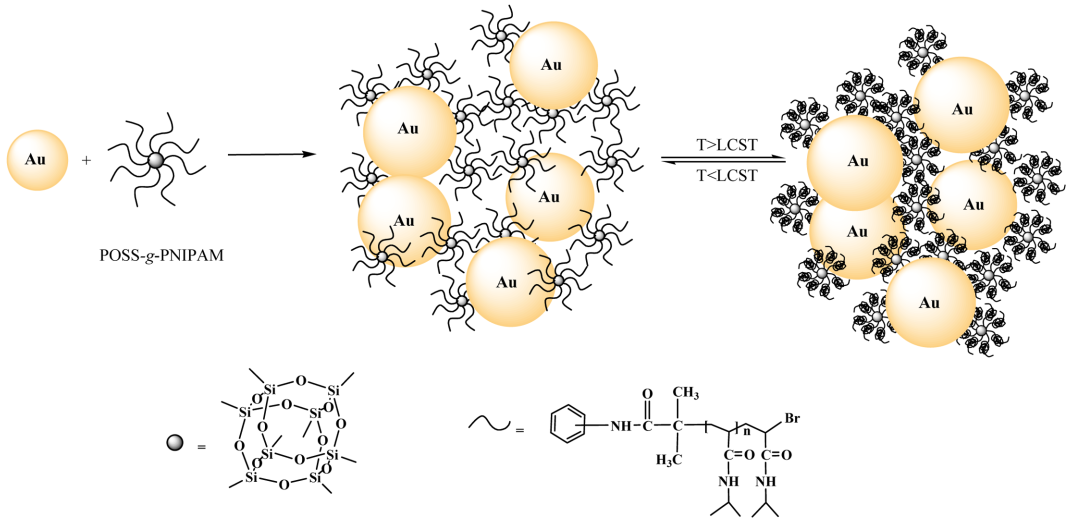
*Corresponding Authors. E-mails: zhangxj@iccas.ac.cn or lrx@haedu.gov.cn



Scheme I. Thermosensitive gold nanoparticles stabilized by POSS-*g*-PNIPAM.

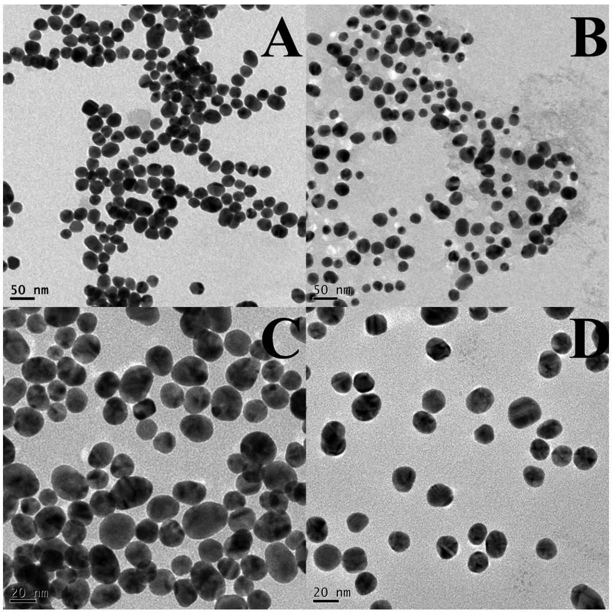


Figure 1. TEM images of (A and C) AuNPs and (B and D) POSS-*g*-PNIPAM stabilized AuNPs.

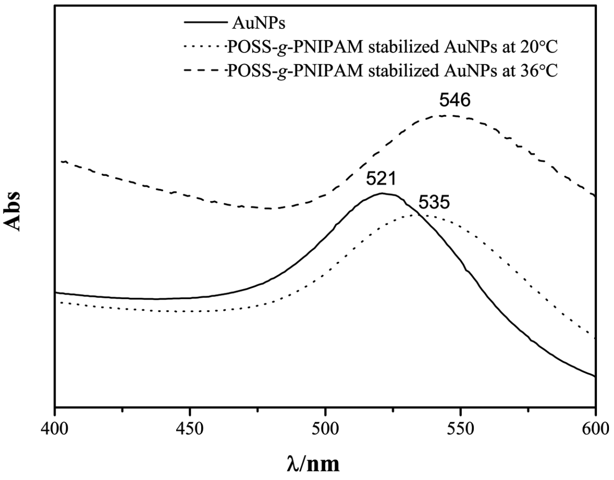


Figure 2. UV-Vis absorption spectra of AuNPs and POSS-*g*-PNIPAM stabilized AuNPs at 20 and 36 °C.

(OPS)[26-28] (Scheme S1). The ATRP of NIPAM can be carried out with OBAPS as initiator in a mixed solvent (DMF/H_2O=2/1) to yield star shaped POSS-*g*-PNIPAM (M_n=1.3×10^4, M_w/M_n= 1.48), which is supported by FTIR, ^{1}H NMR, and GPC results (Figures S1-S3). Gold nanoparticles were synthesized in the presence of sodium citrate with the average diameter of about 20 nm, while they tend to aggregate into cluster after dried (Figure 1(A) and (C)). POSS-*g*-PNIPAM stabilized AuNPs exhibit good dispersion and the suppression of agglomeration (Figure 1(B) and (D)). The molar ratio between POSS-*g*-PNIPAM and AuNPs is calculated about 2.19:1. The result means that there are about two or three POSS-*g*-PNIPAM molecules to stabilize one gold atom on the average level. On the other hand, citrate-stabilized AuNPs have characteristic surface plasma resonance at 521 nm. However, a significant red shift to 535 nm was observed for the SPR of POSS-*g*-PNIPAM stabilized AuNPs (Figure 2). The red shift of AuNPs SPR band was also reported by Shen,[12] which is considered as the result of an increase of the local refractive index change after coating with responsive polymers. Furthermore, the SPR absorptions of POSS-*g*-PNIPAM stabilized AuNPs also have temperature dependence (Figure S4). They continue to have a red shift when increasing the temperature and reach to 546 nm at 36 °C, above their LCST.

Although POSS-*g*-PNIPAM can stabilize AuNPs effectively, the interaction occurs between them is still uncertain. A lot of polymers have been used to protect AuNPs from aggregation through either chemisorption or physisorption

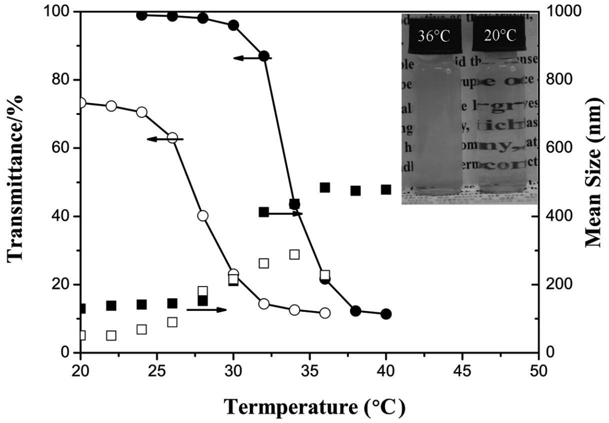


Figure 3. Thermoresponsive changes in transmittance of 95 nM POSS-*g*-PNIPAM solution (solid circles) and POSS-*g*-PNIPAM stabilized AuNPs suspension (open circles); The mean diameters of POSS-*g*-PNIPAM (solid squares) and thermosensitive AuNPs (open squares) at different temperatures, determined by dynamic light scattering (DLS). Inset: photographs of aqueous solutions of POSS-*g*-PNIPAM at 20 °C and after heating up to 36 °C.

way.[6] In chemisorption, most of the polymers used to protect AuNPs contain sulfur atoms/groups that possess strong affinities to gold, which has usually been referred to as covalent binding between sulfur and the Au nano-core. On the other hand, physisorption is defined that the protection of AuNPs with polymers that do not have specific atoms/groups such as sulfur, into which water-soluble polymers, block copolymer micelles, star block copolymers, or nanoreactors are usually used as the stabilizers of AuNPs. However, it seems that no chemisorption exists in the POSS-*g*-PNIPAM polymer and AuNPs system due to the absence of specific strong interactions such as Au-S bond between them. The POSS core is hydrophobic and has strong tendency to aggregate in water, and the POSS-*g*-PNIPAM assemble into 130 nm clusters at 20 °C (Figure 3). So the authors postulate that the POSS-*g*-PNIPAM cluster with a hydrophobic microsection inside might act as a steric stabilizer to prevent AuNPs to aggregate. There are also a few reports that the hydrophobic blocks in star block polymers such as PEO-PPO-PEO[29] and PEO-*b*-PCL[30] can be used to stabilize AuNPs.

Beside good stability, POSS-*g*-PNIPAM stabilized AuNPs also exhibit remarkable thermosensitivity as indicated in their optical transmittance switching property at 500 nm. Figure 3 shows typical plots of the temperature dependence of thermosensitive POSS-*g*-PNIPAM and AuNPs optical transmittance. At 25 °C, POSS-*g*-PNIPAM solution (3 mg/mL) is transparent and the transmittance is close to 100%. The POSS-*g*-PNIPAM solution transmittance decreases to 10% and becomes opaque as increasing temperature to 40 °C. The transmittance of POSS-*g*-PNIPAM stabilized AuNPs solution decreases from 77% to 10% when increasing temperature from 20 to 36 °C, which indicates that the incorporation of POSS-*g*-PNIPAM endows AuNPs with thermosensitivity. The transmittance decrease of POSS-*g*-PNIPAM solution and its AuNPs solution is resulted from the conformation change of PNIPAM chain as increasing the temperature. At 20 °C, water is a good solvent for PNIPAM on AuNPs and polymer chains extend fully due to their hydrophilic character; AuNPs is about 20 nm and its suspension appears as a relative transparent solution. When temperature increases, water becomes a poor solvent for polymer and the hydrogen bond between polymer and water is broken. Then, polymer chains collapse and turn to be hydrophobic. As a result, POSS-*g*-PNIPAM stabilized AuNPs aggregate into clusters (228 nm at 36 °C determined by DLS) and the solution becomes opaque subsequently. The LCST of POSS-*g*-PNIPAM is found at 33.4 °C. Meanwhile, the LCST of POSS-*g*-PNIPAM stabilized AuNPs is at 27.0 °C, lower than that of POSS-*g*-PNIPAM. The decrease in LCST was also found in other PNIPAM stabilized AuNPs systems.[9,12] This result has been explained that the conformational freedom of POSS-*g*-PNIPAM is reduced greatly after immobilization on AuNPs surface, so when POSS-*g*-PNIPAM undergoes a transition from an extended hydrophilic chain to a globular hydrophobic structure, it will collapse only toward AuNPs. On the other hand, AuNPs will restrain thermosensitive polymer cluster within a spherical space, making the hydrophilic to hydrophobic transition easier.

Moreover, the aggregation of POSS-*g*-PNIPAM stabilized AuNPs induced by temperature variation is completely reversible. Figure 4 shows the change of transmittance as POSS-*g*-PNIPAM stabilized AuNPs suspension undergoes heat-cool cycles between 20 and 36 °C. The transmittance of POSS-*g*-PNIPAM stabilized AuNPs suspension changes reversibly between 77% and 10%. The result indicates that the thermosensitive AuNPs are very stable and possess potential for application as temperature sensors.

In summary, we have synthesized a novel star-shaped

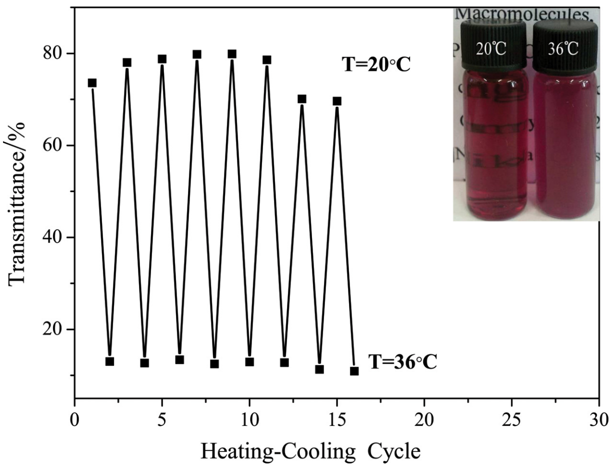


Figure 4. Changes of transmittance of thermosensitive AuNPs suspension during heating-cooling cycles between 20 and 36 °C; Inset: photographs of thermosensitive AuNPs suspension at 20 °C and after heating up to 36 °C.

PNIPAM *via* ATRP with a POSS initiator and used it as a stabilizer of AuNPs. The POSS-*g*-PNIPAM stabilized AuNPs show thermosensitivity with LCST at 27.0 °C. The thermosensitive AuNPs exhibit a reversible clear-opaque transition and their SPR adsorption also shows obvious temperature dependence. They can be used potentially as temperature sensors and drug delivery systems for controlled release.

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Supporting Information: Experimental procedure for the synthesis of POSS-*g*-PNIPAM, its FTIR, ^{1}H NMR and GPC data, as well as the synthesis of AuNPs and its UV-vis spectra temperature dependence after mixing with POSS-*g*-PNIPAM. The materials are available *via* the Internet at http://www.springer.com/13233.

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