

## Thermosensitive Gold Nanoparticles

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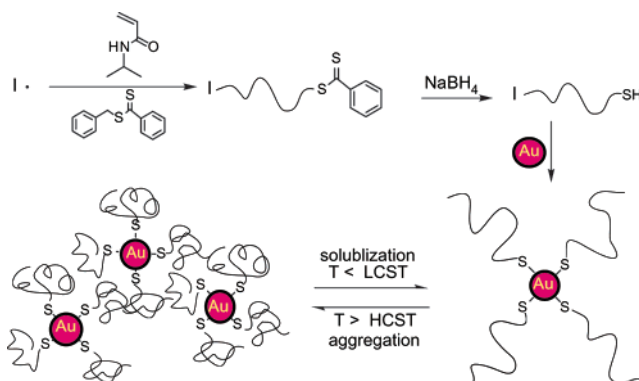
Nanotechnology has experienced a rapid growth recently because nanoparticles exhibit physical and chemical properties that are quite different from those of the bulk solid.<sup>1</sup> Typically, an organic layer comprised of a surfactant<sup>2</sup> or a polymer<sup>3</sup> is anchored at the interface to both localize the nanoparticle and stabilize its properties. Of particular interest is the conjugation of gold nanoparticles with functional macromolecules such as saccharide<sup>4</sup> and oligo deoxyribonucleic acid (DNA).<sup>5</sup> The combination of organic functionality coupled with the dielectric properties of gold nanoparticles has resulted in a new material that provides for sensitive colorimetric detection of polynucleotides.<sup>6</sup> We report here the introduction of thermosensitive polymers onto Au nanoparticles so that the polymer-bound gold nanoparticles now become responsive to temperature.

Poly(*N*-isopropylacrylamide) (PPA) exhibits a low critical solution temperature (LCST) transition from 30 to 45 °C.<sup>7</sup> The polymer is hydrophilic and soluble in water below the LCST, but becomes hydrophobic and forms a macroscopic coacervate phase above that temperature due to the fluctuation of hydrophobic interactions and hydrogen bonding.<sup>8</sup> Anchoring PPA on Au nanoparticles might enhance or amplify such phase-switching behavior unless the interactions between the soft polymer and hard metal nanoparticle negate the thermoresponsive properties. Conjugation with Au nanoparticles requires that the polymer should bear a thiol group at one terminus.<sup>9</sup> We adopt the strategy to use reversible addition-fragmentation chain transfer (RAFT) techniques to polymerize *N*-isopropylacrylamide (iPA) into the well-defined thermosensitive PPA.<sup>10</sup> Using *S*-benzyl dithiobenzoate as the RAFT agent, we have prepared a PPA homopolymer terminated with dithioester groups (Scheme 1). Reduction of dithioester with sodium borohydride provides the thiol group necessary for chemically attaching the thermosensitive polymer on the surface of the as-synthesized Au nanoparticle.

Gold nanoparticles (~13 nm) synthesized in the presence of sodium citrate<sup>11</sup> show uniform size distribution (Figure 1A), but they tend to aggregate into clusters or lines when dried. PPA-tethered Au nanoparticles, however, show potential long-term stability as indicated by good dispersion and the lack of agglomeration (Figure 1B). Both citrate-stabilized and PPA-tethered Au nanoparticles have a red color and characteristic plasmon resonance band for 13-nm Au particles at ~520 nm.<sup>11b</sup>

The 13-nm Au nanoparticles coated with thiol-terminated PPA ( $M_n \approx 4600$ ,  $M_w/M_n \approx 1.48$ ) show remarkable temperature sensitivity as manifested in their optical transmittance switching property at 600 nm. Figure 1C shows typical plots of the temperature-dependent optical transmittance of thermosensitive Au nanoparticles at 0.59 nM along with the mean aggregation diameter. The transition temperature or the inflection point of the transmittance–temperature curve is  $T_t = 28.4$  °C for thermosensitive

Scheme 1

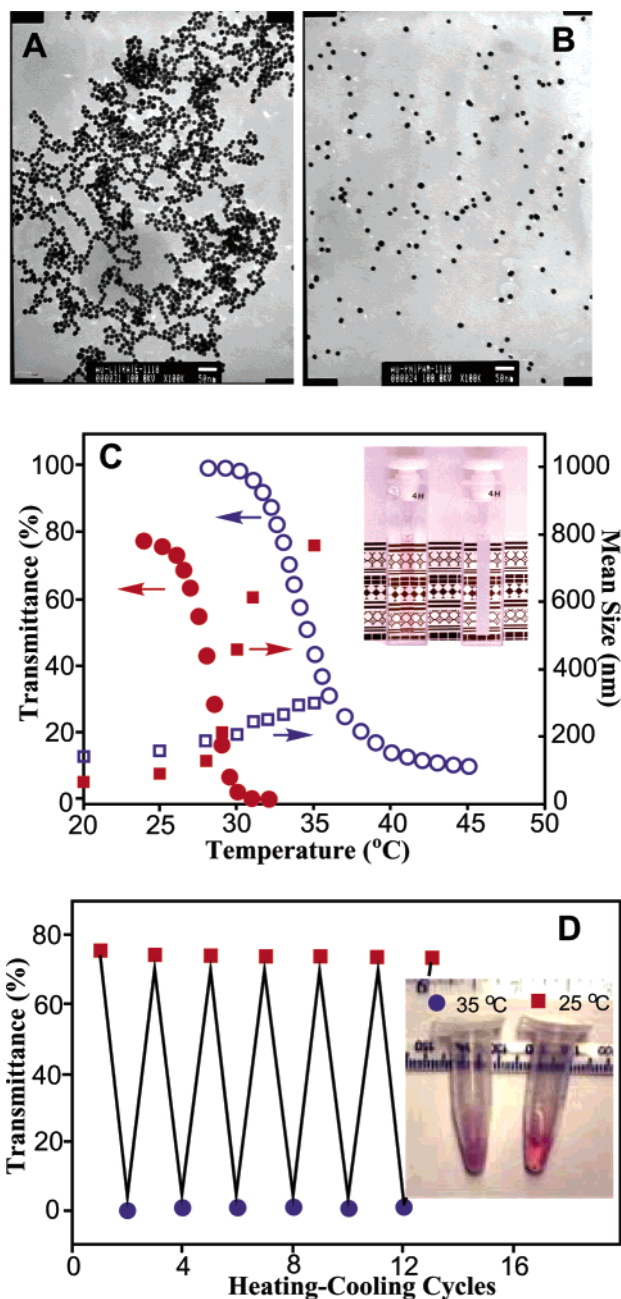


nanoparticles and  $T_t = 33.5$  °C for PPA polymer. A physical mixture of Au nanoparticles with polymer bearing no thiol terminal group has a transition temperature of 33.3 °C. Thermosensitive Au nanoparticles have a sharper transparent-to-opaque transition as indicated by the transition span; the full-width at half-maximum of the first derivative of the transmittance–temperature curve is narrower for thermosensitive Au nanoparticles (2.6 °C) than that of the pure polymers (4.0 °C). The onset occurs at 25 °C and completes at 30 °C for thermosensitive Au nanoparticles, whereas it starts at 30 °C and completes at 45 °C with residual 10% transmittance for PPA (Figure 1C). Below  $T_t$ , the thermosensitive gold nanoparticles have a measurable scattering mean diameter <50 nm, and the transmittance is about 80%. At high temperatures, aggregates up to 800 nm are observed, and the solution becomes completely opaque with transmittance <1%.

The Rayleigh scattering of polymers contributes to an order of magnitude change in transmittance (~100% to 10%), which was further amplified by the strengthening and broadening of the surface plasmon resonance band of the chemically bound gold nanoparticles (10% to <1%). The origin of this amplification effect comes from the fact that one end of the polymer chain is anchored to the gold nanoparticle. When a polymer bound to a nanoparticle undergoes a transition from an extended hydrophilic chain to a globular hydrophobic structure, it will collapse in only one direction, that is, toward the nanoparticle. Moreover, a nanoparticle effectively confines a cluster of thermosensitive polymers within a spherical space, making the hydrophilic to hydrophobic transition easier.<sup>12</sup> Below 25 °C, water is a relatively good solvent for PPA polymer on gold nanoparticles and polymer chains are mostly extended; therefore, the suspension of the gold nanoparticles appears as a transparent solution. In the transition regime, water becomes a poor solvent as polymer–water H-bonds are broken and PPA undergoes conformation changes and exposes much of its hydrophobic surface, including both intrachain “coil-to-globule” transitions and interchain self-association.<sup>13</sup> Intrachain collapse causes the individual polymer to become hydrophobic, while interchain self-association within a single nanoparticle drives the surface of the nanoparticle to switch

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**Figure 1.** TEM images of (A) citrate-stabilized and (B) PPA-tethered Au nanoparticles ( $\sim 13$  nm; scale bar: 50 nm). Thermoresponsive changes in transmittance of 0.59 nM PPA-functionalized Au nanoparticles (solid circle) and PPA (open circles) switch from opaque to transparent ((C) and inset). The mean diameters of thermosensitive Au nanoparticles (solid squares), measured by dynamic light scattering (DLS), increase more dramatically than that of PPA polymer (open squares) at  $T_t$ . The solution switches reversibly (D) from a slightly purple opaque suspension (Au plasmon resonance band 566 nm; v. broad) to a transparent red solution<sup>6a</sup> with normal Au plasmon resonance band at 527 nm (D: inset) between 35 °C (circles) and 25 °C (squares).

from hydrophilic to hydrophobic. Of particular importance is that nanoparticles with hydrophobic surfaces self-aggregate in water. As a result, optical transmittance is dramatically reduced. Above 30 °C, self-organization of nanoparticles attains a new equilibrium as stable cloudy colloids, the switching of the polymer chain conformation is complete, and optical transmittance levels off.

Interestingly, the opaque suspension does not precipitate, and this temperature-dependent clear–opaque transition of the thermosensitive gold nanoparticles is completely reversible (Figure 1D). The suspension is transparent at temperatures below 25 °C and becomes opaque at temperatures above 30 °C. In the transition regime, the optical transparency is a function of temperature. Figure 1D shows the response of optical transparency as the thermosensitive gold nanoparticle suspension undergoes several heat–cool cycles between 35 and 25 °C. The optical transparency changes reversibly between  $\sim 75\%$  and  $\sim 0\%$  transmittance.

In conclusion, we have synthesized thermosensitive gold nanoparticles, exhibiting a sharp, reversible, clear–opaque transition in solution between 25 and 30 °C. Such thermosensitive gold nanoparticles can be potentially fabricated into “smart” liquid cell windows that block the solar heat by turning transparent windows opaque at high temperature. Thus, thermosensitive Au nanoparticles may have potential use for stimuli-responsive applications.

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**Supporting Information Available:** Synthesis, methods, and controls (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Steigerwald, M. L.; Alivisatos, A. P.; Gibson, J. M.; Harris, T. D.; Kortan, R.; Muller, A. J.; Thayer, A. M.; Duncan, T. M.; Douglass, D. C.; Brus, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 3046. (b) Alivisatos, A. P.; Harris, T. D.; Brus, L. E.; Jayaraman, A. *J. Chem. Phys.* **1988**, *89*, 5979. (c) Olshavsky, M. A.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 9438. (d) Alivisatos, A. P. *Science* **1996**, *271*, 933.
- (2) (a) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801. (b) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27. (c) Zhou, Y.; Itoh, H.; Uemura, T.; Naka, K.; Chujo, Y. *Langmuir* **2002**, *18*, 277.
- (3) (a) Mossmer, S.; Spatz, J. P.; Moller, M.; Aberle, T.; Schmidt, J.; Burchard, W. *Macromolecules* **2000**, *33*, 4791. (b) Miyazaki, A.; Nakano, Y. *Langmuir* **2000**, *16*, 7109.
- (4) de la Fuente, J.; Barrientos, A. G.; Rojas, T. C.; Rojo, J.; Canada, J.; Fernandez, A.; Penades, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2257.
- (5) (a) Cao, Y.-W.; Jin, R.; Mirkin, C. A. *J. Am. Chem. Soc.* **2001**, *123*, 7961. (b) Li, Z.; Jin, R.; Mirkin, C. A.; Letsinger, R. L. *Nucleic Acids Res.* **2002**, *30*, 1558. (c) Storhoff, J. J.; Lazarides, A. A.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L.; Schatz, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4640.
- (6) (a) Elghariani, R.; Storhoff, J. J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. *Science* **1997**, *277*, 1078. (b) Nie, S. M.; Emery, S. R. *Science* **1997**, *275*, 1102.
- (7) (a) Heskins, M.; Guillet, J. E. *J. Macromol. Sci., Chem.* **1968**, *A2*, 1441. (b) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379. (c) Wu, C.; Zhou, S. Q. *Macromolecules* **1995**, *28*, 5388. (d) Akiyoshi, K.; Kang, E. C.; Kurumada, S.; Sunamoto, J.; Principi, T.; Winnik, F. M. *Macromolecules* **2000**, *33*, 3244.
- (8) (a) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163. (b) Winnik, F. M. *Polymer* **1990**, *31*, 2125.
- (9) Lowe, A. B.; Sumerlin, B. S.; Donovan, M. S.; McCormick, C. L. *J. Am. Chem. Soc.* **2002**, *124*, 11562.
- (10) Ganachaud, F.; Monteiro, M. J.; Gilbert, R. G.; Dourges, M.-A.; Thang, S. H.; Rizzardo, E. *Macromolecules* **2000**, *33*, 6738.
- (11) (a) Frens, G. *Nat. Phys. Sci.* **1973**, *241*, 20. (b) Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735. (c) Brown, K. R.; Walter, D. G.; Natan, M. J. *Chem. Mater.* **2000**, *12*, 306.
- (12) (a) Li, A. D. Q.; Wang, W.; Wang, L. Q. *Chem.-Eur. J.* **2003**, *9*, 4594. (b) Wang, W.; Wan, W.; Zhou, H. H.; Niu, S. Q.; Li, A. D. Q. *J. Am. Chem. Soc.* **2003**, *125*, 5248. (c) Wang, W.; Han, J. J.; Wang, L. Q.; Li, L. S.; Shaw, W. J.; Li, A. D. Q. *Nano. Lett.* **2003**, *3*, 455. (d) Wang, W.; Li, L. S.; Helms, G.; Zhou, H. H.; Li, A. D. Q. *J. Am. Chem. Soc.* **2003**, *125*, 1120.
- (13) (a) Wang, J. P.; Gan, D. J.; Lyon, L. A.; El-Sayed, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 11284. (b) Jones, C. D.; Lyon, L. A. *Macromolecules* **2003**, *36*, 1988.

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