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Facile Preparation of Transition Metal Nanoparticles Stabilized by Well-Defined (Co)polymers Synthesized via Aqueous Reversible Addition-Fragmentation Chain Transfer Polymerization[†]

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Thiol-stabilized nanoparticles, in particular gold nanoparticles (Au-NPs), have been the focus of intense interest recently because of their potential in fields such as optics and electronics.[1] There are many examples of small molecule stabilization utilizing alkanethiols on a variety of metal species including gold,[2] palladium,[3] and iridium.[3] Recently, research efforts have been directed toward the application of polymeric stabilizing species for metal nanoparticles. For example, de la Fuente et al. reported the use of thiol-derivatized oligosaccharides for the preparation and stabilization of Au-NPs in water,[4] and Mirkin and co-workers have reported DNA-gold nanoparticle conjugates.[5] Synthetic (co)polymers have also been shown to be effective stabilizers. Mayer and Mark investigated various water-soluble homopolymers and random copolymers to stabilize Au-NPs via physical adsorption.[6] Au-NPs decorated with well-defined, covalently bound (co)polymers of controlled architecture could be synthetically tailored to offer increased stabilization along with specific chemical properties. Toward this end, Corbierre et al. reported the covalent attachment of thiol end-capped polystyrene prepared by anionic polymerization to Au-NPs by a “grafting-to” mechanism.[7] The “grafting-from” approach has been employed by Nuss et al. via the atom transfer radical polymerization of *n*-butylacrylate chains from a layer of initiator that had been covalently bound to the surface of Au colloids.[8] Both of the latter examples utilized controlled polymerizations to produce well-defined polymer-stabilizing monolayers. Herein, we describe a novel route for the facile preparation of (co)polymer-stabilized transition metal nanoparticles, via the “grafting-to” approach. Significantly, the (co)polymers employed as stabilizers have been synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization in aqueous media.[9] RAFT is an extremely versatile controlled free radical polymerization technique that operates via a degenerative transfer mechanism, in which thiocarbonylthio compounds act as the chain transfer agents. By virtue of this mechanism, (co)polymers prepared by this technique bear dithioester end groups. The simultaneous reduction at ambient temperature of these dithioester end groups to thiols, in aqueous media in the presence of a suitable transition metal complex or metal sol, leads to the formation of the (co)polymer-stabilized metal nanoparticles; see Scheme 1. Table 1 gives a summary of the molecular weights, polydispersities, and compositions, where applicable, of the (co)polymers utilized for this study. Four water-soluble (co)polymers were initially evaluated: poly(sodium 2-acrylamido-2-methyl propane sulfonate) (PAMPS),[10] poly((*ar*-vinylbenzyl)trimethylammonium chloride) (PVBTAC),[11] poly(*N*,*N*-dimethylacrylamide) (PDMA),[12] and poly(3-[2-*N*-methylacrylamido)-ethyl dimethyl ammonio propane sulfonate-*block*-*N*,*N*-dimethylacrylamide) (PMAEDAPS-*b*-PDMA).[13] This group of (co)polymers is thus composed of an anionic, cationic, neutral, and zwitterionic (betaine) species.

Scheme 1. Preparation of (Co)polymer-Stabilized Transition Metal Nanoparticles

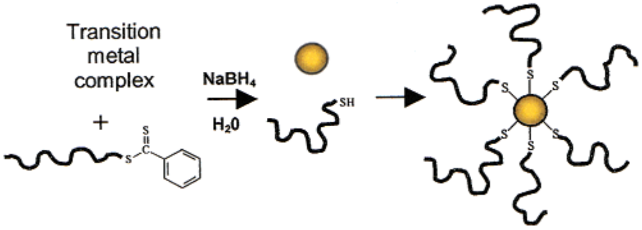

Table 1. Summary of the Molecular Characteristics of the RAFT-Synthesized (Co)polymers Employed as Stabilizing Species

polymer	M_n[a]	M_w/M_n[a]	composition
PAMPS (P1)	17 700[b]	1.27	
PVBTAC (P2)	10 500[c]	1.06	
PDMA (P3)	29 100[d]	1.18	
P(MAEDAPS-*b*-DMA) (P4)	58 700[b]	1.19	35:65[e] MAEDAPS:DMA

[a] As determined by aqueous size exclusion chromatography. [b] Reported as $PNaSSO_3$ equivalents. [c] Reported as P2VP equivalents. [d] Absolute MW as determined by on-line light scattering (Wyatt DAWN EOS + Optilab RI detector). [e] As determined by ^1H NMR spectroscopy.

(Co)polymer-stabilized nanoparticles based on Au ($HAuCl_4$ sol), Ag ($AgNO_3$), Pt ($Na_2PtCl_6 \cdot 6H_2O$), and Rh (Na_3RhCl_6) have been prepared, using a 0.01 wt % solution of the appropriate salt and a 1.0 M aqueous solution of $NaBH_4$ as the reducing agent (molar ratio of $NaBH_4$:dithioester end groups was 25:1). A portion of the reaction mixture was centrifuged for 1 h at 13 000 rpm, and the supernatant was removed. The resulting aggregates were redispersed in deionized water by agitation. The centrifugation and redispersal process was repeated several times to ensure that only covalently bound polymers remained in the colloidal solutions of the stabilized nanoparticles.

Transmission electron microscopy (TEM) was employed to examine the metal nanoparticles after stabilization. As representative examples, Figure 1 shows the TEM micrographs for a series of Au-modified colloids.

Figure 1b clearly shows that when the reduction is performed in the absence of the RAFT synthesized (co)polymer, the reduced metal species simply flocculates (precipitation is observed). When

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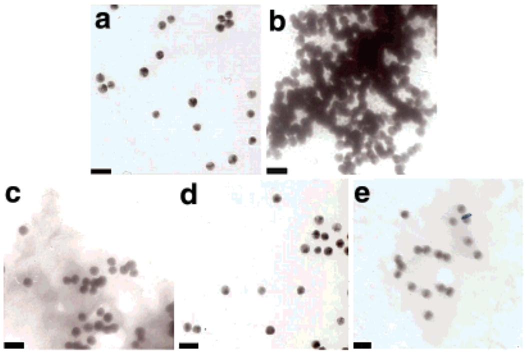

Figure 1. TEM micrographs of Au sol (a), reduced Au sol (b), P1-stabilized Au-NPs (c), P2-stabilized Au-NPs (d), and P3-stabilized Au-NPs (e). Scale bars correspond to 40 nm.

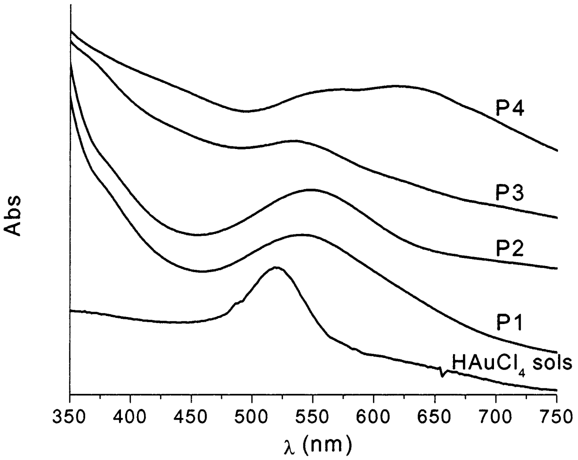

Figure 2. UV−vis spectra for HAuCl$_4$ sols and polymer-stabilized Au-NPs. The curves have been spaced to allow for better viewing.

the reduction takes place in the presence of the polymers P2−P4, extremely stable colloids are formed.

Approximately 9 weeks after preparation, under an air atmosphere, the gold colloidal solutions are still stable with little or no sign of flocculation. P1-stabilized Au-NPs (anionic polymer) are not as stable as the others and flocculate readily within 48 h. However, they are very easily redispersed by simple agitation. Interestingly, given the betaine nature of the P4 copolymer, the metal nanoparticles are *only* stable in the presence of salt (NaBr in this case). For this reason, TEM of the P4-stabilized Au-NPs was not attempted due to the interference of the NaBr crystals that remained on the grids following evaporation of the solvent.

UV−vis spectroscopy was used to characterize the original unconjugated gold sols and the polymer-stabilized nanoparticles; see Figure 2. The spectrum of the unconjugated gold sols (prior to reduction) shows the characteristic absorption at 523 nm attributable to plasmon resonance. The spectra of the polymer-stabilized colloidal solutions after a period of 9 weeks show a slight red shift ($\lambda_{\max} = 533$ nm) indicative of a small amount of aggregation to form particles greater than 50 nm.[14,15] Given that the original size of the unmodified colloids, as determined by TEM, was 20 nm, this increase in $\lambda_{\max}$ is not surprising. The more significant red shift observed for the P4-stabilized nanoparticles is attributed to salt-induced aggregation, which results from the NaBr required to solubilize the betaine block of the copolymer.[13]

The presence of polymer-stabilized nanoparticles prepared from other transition metal complexes, such as AgNO$_3$, was confirmed by both TEM and visual inspection. The colloidal solutions of these metal nanoparticles were homogeneous with colors dependent on the metal being stabilized. For instance, prior to reduction, the solution of AgNO$_3$ and P2 was slightly orange due to the presence of the terminal dithiobenzoate functionality of the polymer. Addition of NaBH$_4$ was accompanied by an immediate color change to an intense greenish-brown. Similar to the micrographs shown in Figure 1, individual P2-stabilized Ag-NPs that were approximately 5−10 nm in diameter were observed by TEM. Similar results were obtained for the polymer-stabilized Pt and Rh colloids. Large aggregates were only observed for the salts reduced in the absence of polymer. In fact, visible precipitate was observed for most of these systems immediately following reduction.

The simultaneous reduction of thiocarbonylthio end-capped (co)-polymer chains and metal salts affords a facile process for the preparation of (co)polymer-stabilized metal nanoparticles. The ability to synthesize (co)polymers in aqueous solution with controlled architectures, predetermined molecular weights, and narrow molecular weight distributions from a wide range of functional monomers makes RAFT an excellent candidate for the synthesis of a plethora of novel well-defined (co)polymer stabilization systems.

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Supporting Information Available: Experimental procedures, selected additional TEMs, and pictures of the polymer-stabilized gold colloids (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) McConnell, W. P.; Novak, J. P.; Brousseau, L. C.; Fuierer, R. R.; Tenent, R. C.; Feldheim, D. L. *J. Phys. Chem. B* **2000**, *104*, 8925−8930.
(2) (a) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17−30. (b) McIntosh, C. M.; Esposito, E. A.; Boal, A. K.; Simard, J. M.; Martin, C. T.; Rotello, V. M. *J. Am. Chem. Soc.* **2001**, *123*, 7626−7629.
(3) Yee, C. K.; Jordan, R.; Ulman, A.; White, H.; King, A.; Rafailovich, M.; Sokolov, J. *Langmuir* **1999**, *15*, 3486−3491.
(4) de la Fuente, J.; Barrientos, A. G.; Rojas, T. C.; Rojo, J.; Cañada, J.; Fernández, A.; Penadés, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2257−2261.
(5) (a) Cao, Y.-W.; Jin, R.; Mirkin, C. A. *J. Am. Chem. Soc.* **2001**, *123*, 7961−7962. (b) Li, Z.; Jin, R.; Mirkin, C. A.; Letsinger, R. L. *Nucleic Acids Res.* **2002**, *30*, 1558−1562.
(6) Mayer, A. B. R.; Mark, J. E. *Eur. Polym. J.* **1998**, *34*, 103−108.
(7) Corbierre, M. K.; Cameron, N. S.; Sutton, M.; Mochrie, S. G. J.; Lurio, L. B.; Rühm, A.; Lennox, R. B. *J. Am. Chem. Soc.* **2001**, *123*, 10411−10412.
(8) Nuss, S.; Böttcher, H.; Wurm, H.; Hallensleben, M. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 4016−4018.
(9) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.
(10) Sumerlin, B. S.; Donovan, M. S.; Mitsukami, Y.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2001**, *34*, 6561−6564.
(11) Mitsukami, Y.; Donovan, M. S.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2001**, *34*, 2248−2256.
(12) (a) Donovan, M. S.; Lowe, A. B.; Sumerlin, B. S.; McCormick, C. L. *Macromolecules* **2002**, *35*, 4123−4132. (b) Donovan, M. S.; Sanford, T.; Lowe, A. B.; Mitsukami, Y.; Sumerlin, B. S.; McCormick, C. L. *Macromolecules* **2002**, *35*, 4570−4572.
(13) Lowe, A. B.; McCormick, C. L. *Aust. J. Chem.* **2002**, in press.
(14) Quinten, M.; Kreibig, U. *Surf. Sci.* **1986**, *172*, 557−577.
(15) Kim, Y.; Johnson, R. C.; Hupp, J. T. *Nano Lett.* **2001**, *1*, 165−167.

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