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ARTICLE TYPE

High thermal stability of block copolymer-capped Au and Cu nanoparticles

Iryna I. Perepichka, Mohamed A. Mezour, Dmitrii F. Perepichka* and R. Bruce Lennox*

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Producing solution-based metal nanoparticles that do not agglomerate at elevated temperatures remains challenging. We show that thermally stable Au and Cu nanoparticles can be prepared using polystyrene–poly(4-vinylpyridine) diblock copolymers as capping agents. These materials remain stable when their solutions are subjected to prolonged heating up to 160°C for more than 48h. These conditions are sufficient for applications in most wet chemistry processes and reactions.

Metal nanoparticles (NP) are widely studied for their applications in medicine,¹ sensing,² data storage,³ conducting inks,⁴ plastic doping,⁵ surface-initiated polymerization,⁶ and catalysis.^{7,8} However, the instability of most NP in solution at elevated temperatures limits many of these applications.⁹ The tendency of unsupported metal nanoparticles to aggregate generally starts with dissociation of the protecting ligands from the NP surface. Alkylthiols are the most commonly used capping agents used to stabilize metal NP, particularly AuNP, in solution.^{10,11} The densely packed thiol monolayer physically and electronically blocks the metal surface from many chemical interactions with the solute. The relatively strong sulfur–gold bond (~44 kcal/mol¹²) offers significant robustness to thiol-protected AuNP at room temperature, although desorption of the ligand can readily occur at elevated temperatures, via disulfide bond formation. Other capping agents, such as amines, phosphines, or tetraalkylammonium halides feature weaker interactions with the metal, which enables an exchange reaction with solvent and/or other ligands and further reduces the stability of NP.¹³ Thus, the weaker binding of pyridine to gold (~22 kcal/mol¹⁴) makes 4-(dimethylamino)pyridine-protected AuNP versatile precursors in ligand-exchange protocols.¹⁵

We are not aware of any report where Au, Ag, or Cu NP remain stable in solution under prolonged heating at >100°C. However, NP stability under conditions of prolonged heating is highly desirable as these conditions are often necessary for application in catalysis and thermoplastic processing of NP/polymer composite materials.

One potential approach to improve the temperature stability of ligand-protected NP is to use multidentate ligands, whose binding constant increases exponentially with the number of surface-coordinating groups.¹⁶ However, using a strongly binding multidentate ligand (e.g., a polythiol) typically leads to aggregation of NP due to cross-linking of the nanoparticles by the ligand.¹⁷ Another possibility is to use a polymer capping agent,

that can suppress both the ligand dissociation, via increased inter-ligand interactions, and collisions of the metal cores.^{18,19} In this respect, use of block copolymers (BC) where one block acts as a ligand and the other block serves as a constituent of the protecting corona may improve the stability of NP in solution.^{20,21} In particular, NP protected with thiol-terminated block copolymers have been extensively studied.²² The use of multifunctional interactions of one of the entire blocks and a metal surface is less explored although not unprecedented.^{23,24} For example, diblock and triblock copolymers with poly(2- or 4-vinylpyridine)^{25,26} or poly(ethylene oxide) (PEO)²⁷ as one of the blocks have been reported to stabilize Au, Pd, Pt and Rh NP, and have also been applied in catalysis.^{28,29} The moderate binding strength of individual pyridine groups¹⁴ allows the metal surfaces to interact with solute, while a chelating effect of the multidentate ligand provides significant stabilization to the NP toward aggregation. The other, non-binding block [often polystyrene^{25,30} or poly(ethylene oxide)^{26,29}] further stabilizes the NP and enables solubility control. Although the preparation and phase behavior of BC/NP complexes in solution has been studied,^{25,26,31,32} their thermal stability has not been reported to date.

We report here the unprecedented stability of Au(0) and Cu(0) NP capped with polystyrene–poly(4-vinylpyridine) (PS-P4VP) diblock copolymers. Despite the absence of strong-binding thiol functionalities, the resulting NP reveal significant long-term stability in solvent at temperatures as high as 160°C over 48 h. Such stability is presented for highly reactive (Cu) and noble (Au) metals, demonstrating the generality of this approach.

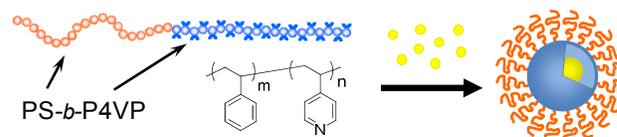


Fig. 1 Illustration of metal nanoparticle formation in a diblock copolymer micelle.

The NP are prepared by reduction of HAuCl₄ or copper (II) 2-ethylhexanoate precursors with BH₃·THF complex, in THF or 1,4-dioxane media, in the presence of PS-P4VP.⁸ In these solvents, PS-P4VP forms micelles with PS coronae and P4VP cores^{33,34} (Figure 1), which should lead to formation of NP incorporated within and protected by a polymer shell layer. Stable NP solutions were obtained over a range of metal–ligand molar

ratios (0.6:1 to 10:1) and for diblock copolymers of different length and functional block fraction ($M_n = 37\text{--}59$ kg/mol; $f_{P4VP} = 12\text{--}59$ mol%: PS₃₈₄-P4VP₅₃; PS₃₉₈-P4VP₁₆₆; PS₁₉₂-P4VP₁₆₂; PS₁₉₁-P4VP₂₈₀).

Solutions of the resulting AuNP have the usual bright pink color associated with AuNP (5–10 nm) and exhibit the characteristic plasmon absorption at λ_{max} 530–540 nm. Solutions of the CuNP are dark brown and have a plasmon absorption at λ_{max} 560–570 nm. TEM-derived diameters of 3–10 nm are observed for these Au and CuNP.

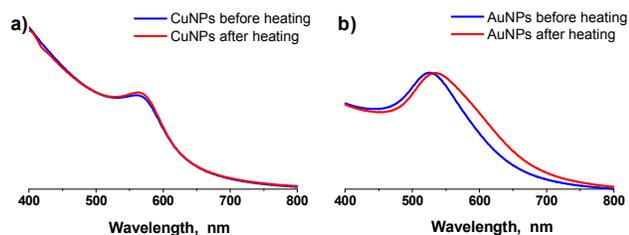


Fig. 2 Normalized UV-vis spectra of (a) PS₁₉₂-P4VP₁₆₂/CuNP and (b) PS₁₉₁-P4VP₂₈₀/AuNP before and after heating in 1,4-dioxane at 160°C for 20 hours.

Both BC/Au and BC/Cu nanoparticle samples are stable in solution at room temperature for months, although strict avoidance of oxygen is required to maintain stability of the CuNP. The change in color of BC/CuNP solutions exposed to air (and the subsequent precipitation of a black copper oxide) indicates that the P4VP-protected surface of NP is readily accessible towards oxidative chemical reagents, which is a necessary condition for their application in catalysis.³⁵ The thermal stability of the BC-protected NP solutions was assessed by heating up to 160°C for 20–48 h in pressure-resistant glass tubes. The solution color remains unchanged under these conditions. The plasmon band in UV-vis spectra of CuNP is practically unaffected by heating although a small red-shift and broadening was observed for AuNP (Fig. 2). The latter can be attributed to effective Ostwald ripening taking place in AuNP at such a high temperature. Control experiments using thiol-terminated polymers (PS-SH [$M_n = 1.7$ kg/mol] and PEO-SH [$M_n = 0.3$ and 2 kg/mol]) or dodecanethiol as ligands show a complete aggregation and precipitation of derived AuNP and CuNP in less than 1 h at 100°C (see ESI†).

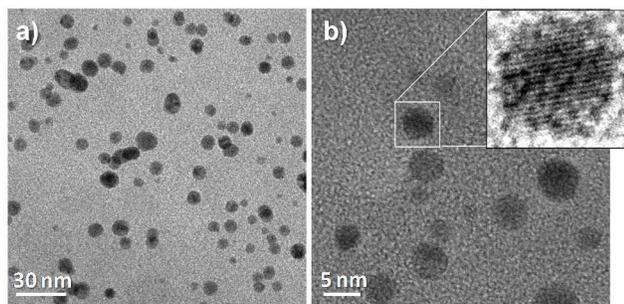


Fig. 3 TEM images of (a) PS₁₉₁-P4VP₂₈₀/AuNP after heating in 1,4-dioxane at 160°C (under pressure) for 20 h, (b) PS₁₉₂-P4VP₁₆₂/CuNP after heating in 1,4-dioxane at 105°C for 20 h.

TEM images confirm that the sizes and shapes of the CuNP do

not significantly change as a result of heating. However, the diameter of the AuNP almost doubles, which is consistent with an Ostwald ripening process (ESI†).³⁶ TEM-based electron diffraction and X-ray photoelectron spectroscopy (XPS) confirm that the nature of the NP remains unchanged, even after prolonged heating. Thus, characteristic of Cu(0) 0.20 nm d(111) lattice spacing (Fig. 3b) and binding energies (Cu^{2p3/2} = 933.0 eV; Cu^{2p1/2} = 952.7 eV, Fig. 4a) are observed for thermally-treated CuNP. A shoulder at 945 eV indicates the presence of a small amount of Cu(I), likely formed during the transfer of the sample into the XPS chamber. Deconvolution of the N 1s XPS signal yields two peaks at 398.8 eV and 400.5 eV at a ratio of ca. 1:3 (Fig. 4b). These are assigned to free and Cu-bonded pyridine moiety, respectively,³⁷ suggesting that ca. 75% of the P4VP units are bonded to the CuNP surface.

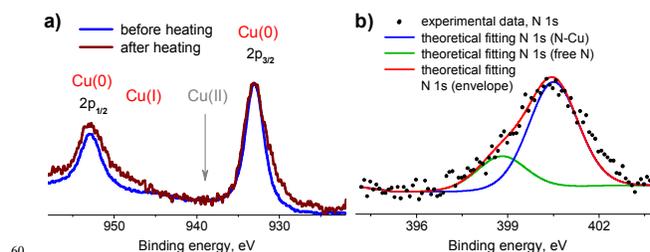


Fig. 4 XPS of PS₁₉₂-P4VP₁₆₂/CuNP: (a) copper 2p XPS spectrum region before and after heating in 1,4-dioxane at 105°C for 20 h; (b) nitrogen 1s XPS spectrum region (before heating).

Remarkably, while typical synthesis of ligand-protected nanoparticles requires a large excess of ligand (vs. metal), in this work equimolar and up to 10-fold excess of metal (Cu:VP = 1.3:1.0 to 10:1, VP – vinylpyridine unit in the BC) was used without compromising the stability of the resulting NP (Fig. 5).

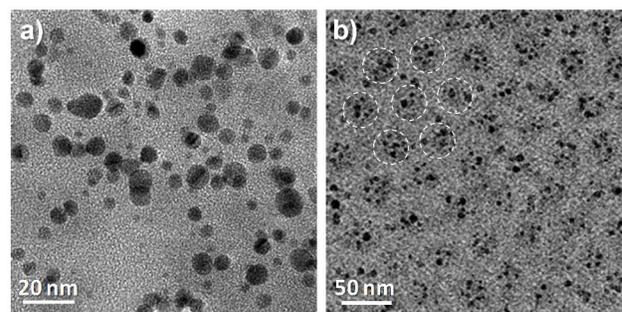


Fig. 5 TEM images of PS₃₉₈-P4VP₁₆₆/CuNP after heating in 1,4-dioxane at 160°C for 20 h. Metal to VP ratio is (a) 1:1, (b) 10:1. Dashed circles in b highlight the boundaries of micelle cores (P4VP) with CuNP inside.

Previous light scattering studies of PS₃₉₈-PVP₁₆₆ in THF establish values of the hydrodynamic radius (R_h) and radius of gyration (R_g) 27.1±0.4 nm and 19.2±4.8 nm, respectively.³⁸ The size of the micelles obviously exceeds the sizes of the NP studied here, and thus multiple metal cores can be accommodated within the same diblock copolymer micelle. Indeed, when the ratio of Cu to BC ligand is increased, the formation of multiple metal cores per micelle becomes obvious in TEM images. The multicore structure remains stable after prolonged heating at 160°C (Fig. 5b). This is in contrast to the similar multicore AuNP/PS-PEO structure, which aggregates into a single metal core per micelle

form after annealing at 90°C.²⁷

In summary, an efficient and facile strategy to prepare thermally stable metal nanoparticles in organic solutions by a one-phase method has been presented. We have shown that gold and copper nanoparticles stabilized by PS-P4VP diblock copolymers remain homogeneously dissolved and unchanged after heating in 1,4-dioxane at 160°C for 2 days. Such conditions are expected to be compatible with many homogeneous catalysis and composite materials applications of nanoparticles. Copper nanoparticles, which are less studied but are attractive due to their low-cost and higher reactivity cf. gold, are of particular practical interest. The stability of the diblock copolymer-capped NP in solution at high temperatures is attributed to a combination of the polydentate ligand (which has significant affinity for the NP surface) and the surrounding polymer matrix (which diminishes the diffusion of the metal cores to the extent that they do not make contact with one another in the experimental timeframe).

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Notes and references

Department of Chemistry, Centre for Self-Assembled Chemical Structures, McGill University, 801 Sherbrooke Str. West, Montreal (QC) H3A 2K6, Canada. Fax: +1 514 398 3797; Tel: +1 514 398 6233; E-mail: dmitrii.perepichka@mcgill.ca, bruce.lemox@mcgill.ca

† Electronic Supplementary Information (ESI) available: experimental details and characterization of AuNP and CuNP. See DOI: 10.1039/b000000x/

§ 1.5–3.0 mg PS-P4VP (Polymer Source, Canada) was dissolved in 10 mL of anhydrous oxygen-free THF or 1,4-dioxane. Copper (II) 2-ethylhexanoate (17–70 μmol) or HAuCl₄·3H₂O (8–15 μmol) was dissolved in the above solution (VP:metal molar ratio is 1:0.6–10) and stirred overnight in a nitrogen-filled glove box. The reducing agent BH₃-THF (0.3–1 mL), 1.0 M in THF was added dropwise to the block copolymer / metal salt solution resulting in gradual change of color to dark brown or dark red indicating the formation of CuNP or AuNP, respectively. The prepared solution of NP was used as is in the presented analysis and stability tests.

- N. T. K. Nguyen and L. A. W. Greena, *Nano Today*, 2010, **5**, 213.
- S. Prakash, T. Chakrabarty, A. K. Singh and V. K. Shahi, *Biosens. Bioelectron.*, 2013, **41**, 43.
- D. Wan, H.-L. Chen, S.-C. Tseng, L. A. Wang and Y.-P. Chen, *ACS Nano*, 2010, **4**, 165.
- S. Jeong, S. H. Lee, Y. Jo, S. S. Lee, Y.-H. Seo, B. W. Ahn, G. Kim, G.-E. Jang, J.-U. Park, B.-H. Ryua and Y. Choi, *J. Mater. Chem. C*, 2013, **1**, 2704.
- H. Maa, Y. Geng, Y.-I. Lee, J. Hao and H.-G. Liu, *J. Colloid Interf. Sci.*, 2013, **394**, 223.
- C. M. Hui, J. Pietrasik, M. Schmitt, C. Mahoney, J. Choi, M. R. Bockstaller, K. Matyjaszewski, *Chem. Mater.*, 2014, **26**, 745.
- H. Cong and J. A. Porco, *ACS Catal.*, 2012, **2**, 65; C. D. Pina, E. Falletta, L. Prati and M. Rossi, *Chem. Soc. Rev.*, 2008, **37**, 2077.
- B. C. Ranu, R. Dey, T. Chatterjee and S. Ahammed, *ChemSusChem*, 2012, **5**, 22.
- A. Cao and G. Vesper, *Nature Materials*, 2010, **9**, 75.
- M. C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293.
- J. C. Azcarate, G. Corthey, E. Pensa, C. Vericat, M. H. Fonticelli, R. C. Salvarezza and P. Carro, *J. Phys. Chem. Lett.*, 2013, **4**, 3127.
- G. Timp, *Nanotechnology*, Springer-Verlag, New York, 1999.
- A. Caragheorghopol and V. Chechik, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5029.

- A. Bilic, J. R. Reimers and N. S. Hush, *J. Phys. Chem. B*, 2002, **106**, 6740.
- S. Rucareanu, V. J. Gandubert and R. B. Lennox, *Chem. Mater.*, 2011, **18**, 4674.
- P. Chinwangso, A. C. Jamison and T. R. Lee, *Acc. Chem. Res.*, 2011, **44**, 511.
- G. Zotti and B. Vercelli, *Chem. Mater.*, 2008, **20**, 397.
- Wuelfing, W. P.; Gross, S. M.; Miles, D. T.; Murray, R. W. *J. Am. Chem. Soc.* **1998**, *120*, 12696; S. Rucareanu, M. Maccarini, J. L. Shepherd and R. B. Lennox, *J. Mater. Chem.* 2008, **18**, 5830;
- J. Shan and H. Tenhu, *Chem. Comm.*, 2007, 4580; M. Yoo, S. Kim and J. Bang, *J. Polym. Sci. Part B: Polym. Phys.*, 2013, **51**, 494.
- M. Filali, M. A. R. Meier, U. S. Schubert and J.-F. Gohy, *Langmuir*, **2005**, *21*, 7995.
- A. Haryono and W. H. Binder, *Small*, 2006, **2**, 600.
- J. J. Chiu, B. J. Kim, E. J. Kramer and D. J. Pine, *J. Am. Chem. Soc.*, 2005, **127**, 5036; S. G. Jang, E. J. Kramer and C. J. Hawker, *J. Am. Chem. Soc.*, 2011, **133**, 16986; M. Yoo, S. Kim, S. G. Jang, S.-H. Choi, H. Yang, E. J. Kramer, W. B. Lee, B. J. Kim and J. Bang, *Macromol.*, 2011, **44**, 9356; S. G. Jang, A. Khan, C. J. Hawker and E. J. Kramer, *Macromol.*, 2012, **45**, 1553; Y. Mai and A. Eisenberg, *Macromol.*, 2011, **44**, 3179.
- Y. Mai and A. Eisenberg, *Acc. Chem. Res.*, 2012, **45**, 1657.
- S. Luo, J. Xu, Y. Zhang, S. Liu and C. Wu, *J. Phys. Chem. B*, 2005, **109**, 22159.
- M. V. Seregina, L. M. Bronstein, O. A. Platonova, D. M. Chernyshov, P. M. Valetsky, J. Hartmann, E. Wenz and M. Antonietti, *Chem. Mater.* 1997, **9**, 923; L. M. Bronstein, S. N. Sidorov, P. M. Valetsky, J. Hartmann, H. Cölfen and M. Antonietti, *Langmuir*, 1999, **15**, 6256.
- S. N. Sidorov, L. M. Bronstein, Y. A. Kabachii, P. M. Valetsky, P. L. Soo, D. Maysinger and A. Eisenberg, *Langmuir*, 2004, **20**, 3543; T. Azzam, L. Bronstein and A. Eisenberg, *Langmuir*, 2008, **24**, 6521; Y. H. Jang, S. T. Kochuveedu, Y. J. Jang, H.-Y. Shin, S. Yoon, M. Steinhart and D. H. Kim, *Carbon*, 2011, **49**, 2120; J. Zhao, X. C. Chen and P. F. Green, *Soft Matter*, 2013, **9**, 6128.
- J. P. Spatz, A. Roescher and M. Möller, *Adv. Mater.*, 1996, **8**, 337.
- M. Antonietti, E. Wenz, L. Bronstein and M. Seregina, *Adv. Mater.*, 1995, **7**, 1000.
- N. Semagina, E. Joanneta, S. Parraa, E. Sulmanb, A. Renkena, L. Kiwi-Minsker, *Appl. Cat. A: General*, 2005, **280**, 141.
- M. Aizawa and J. M. Buriak, *Chem. Mater.*, 2007, **19**, 5090.
- L. Bronstein, E. Krämer, B. Berton, C. Burger, S. Förster and M. Antonietti, *Chem. Mater.*, 1999, **11**, 1402.
- C.-T. Lo, B. Lee, R. E. Winans and P. Thiyagarajan, *Macromol.*, 2006, **39**, 6318; S. Voldent, A.-L. Kjøniksen, K. Zhu, J. Genzer, B. Nyström and R. Glomm, *ACS Nano*, 2010, **4**, 1187.
- M. Antonietti, S. Heinz, M. Schmidt and C. Rosenauer, *Macromol.*, 1994, **27**, 3276.
- S. P. Nunes, M. Karunakaran, N. Pradeep, A. R. Behzad, B. Hooghan, R. Sougrat, H. He and K.-V. Peinemann, *Langmuir*, 2011, **27**, 10184.
- D. Astruc, *Tetrahedron: Asymmetry*, 2010, **21**, 1041.
- S. T. Gentry, S. F. Kendra and M. W. Bezpalko, *J. Phys. Chem. C*, 2011, **115**, 12736.
- D. E. Diaz-Droguetta, R. Espinoza and V. M. Fuenzalida, *Appl. Surf. Sci.*, 2011, **257**, 4597.
- S. Roland, D. Gaspard, R. E. Prud'homme, C. G. Bazuin, *Macromol.*, 2012, **45**, 5463.