Stable, Monolayer-Protected Metal Alloy Clusters

Michael J. Hostetler,*,† Chuan-Jian Zhong,‡ Brian K. H. Yen,†
Jim Anderegg,† Stephen M. Gross,† Neal D. Evans,§
Marc Porter,‡ and Royce W. Murray*,†

Kenan Laboratories of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27599-3290
Department of Chemistry, Iowa State University
Ames, Iowa 50011-3111
Oak Ridge Institute for Science and Education
P.O. Box 117, Oak Ridge, Tennessee 37831

Alloy particles[1] can exhibit electronic,[2-4] optical,[5-10] and catalytic properties[11,12] that are distinct from those of the corresponding mono-metal particles,[13-17] prompting numerous preparations of multi-metal nanoparticles, including those that can be considered core/shell bimetallic, partially segregated alloy, and pure alloy.[1-12] These earlier alloy particles typically required specialized equipment or handling procedures, posed difficulties in isolation and analysis, and could not be redissolved in air-stable forms.

This paper describes a simple synthesis of nanometer-sized monolayer-protected alloy clusters (MPACs) that are the first examples of stable, large, alloy molecules that can be isolated in solvent-free forms and redissolved without change. The stable alkanethiolate monolayer is the key to preventing metal core aggregation. The MPAC core compositions can be systematically varied in regards to ratios and numbers of groups 10 (Pt, Pd) and 11 (Cu, Ag, Au) metals, creating a pathway to studying the properties of monolayer-protected metal clusters over a continuum of alloy compositions and monolayer functionalities.[13]

The relatively simple procedures described first for mono-metal gold[14] and then for silver[15] MPCs were used to prepare the binary and higher group 10/10 and 10/11 metal MPACs listed in Table 1. All contain Au as one of the metals. Briefly, the appropriate metal salts (metal−thiolate polymers prepared from metal salts), dissolved or dispersed in a toluene/water biphasic solution, are reduced by $NaBH_4$ in the presence of a phase-transfer catalyst (Oct_4NBr) and a 3-fold excess (relative to Au) of either dodecanethiol or didodecyl disulfide. The isolated MPAC products are air and moisture stable and generally obtained in high yield.

MPAC core sizes, compositions, and thermal stabilities as assessed[16a] by transmission electron microscopy (TEM) and ^{1}H NMR line broadening, X-ray photoelectron spectroscopy (XPS) and elemental analysis, and thermogravimetry (TGA), respectively, are summarized in Table 1. TEM shows that Pd/Au MPAC cores (Figure 1a) are small and relatively monodisperse (1.7 nm, av, ~20% dispersity), while most Ag/Au MPAC cores (Figure 1b) are larger (3.2 nm, a small core population[18] is also present). Other MPACs were of intermediate size. For comparison, similarly prepared mono-metal Au MPCs have core diameters of 2.0 nm (av, ~20% dispersity).[16a] Elemental and XPS analyses shows that *overall* MPAC core metal ratios vary with, but differ from, the metal salt feed ratio, and that incorporation of the more noble metal into the core is favored. Galvanic effects may be in part responsible for the differential incorporation; for example, in Ag/Cu mixtures the Cu core content could be depressed by Cu^0 acting as an ancillary reductant of Ag^+, which leaches Cu^0 from the nascent core.

The spatial distribution of the metals in the MPAC cores is another important issue; do core−shell structures, partially segregated alloys, or pure alloys dominate, and does the ligand monolayer influence the core structure? Partially segregated alloys are a common motif of previous work.[1,8] The more noble metals tend to prefer nonsurface sites,[10] but pure alloy structures have also been observed[10] for AgPd nanoparticles. Table 1 shows (TGA data) that the MPACs are generally more thermally stable than the corresponding mono-metallic MPCs, and significantly, the presence and proportion of certain metals enhances stability (Ag) or instability (Cu). Such results are in line with metal−SR bond strengths[19] and with segregation of the less noble metal to the MPAC core surface. XPS S2p data (from the dodecanethiolate ligands, details in Supporting Information) help to quantify this conclusion. All alloy MPACs display at least two $S2p_{1/2,3/2}$ doublets, implying that all alloys have at least two metal surface constituents (i.e., the alloy is not strictly core−shell but rather only partially surface segregated). The binding energies (BE) of two S2p doublets can be associated with values characteristic of dodecanethiolate-protected mono-metal clusters; this is most cleanly done for Au/Ag and Au/Cu MPACs, where the Au S2p doublet displays the higher BE. These assignments and the relative areas of the S2p doublets produce the relative MPAC core surface populations shown in Table 1. The results are striking for the series of Au/Ag MPACs, where clearly Ag prefers cluster *surface* sites to the extent of ca. 60% in $AuAg_{0.4}$ MPAC cores and ca. 86% for $AuAg_{2.5}$ MPAC cores.

Figure 2 shows that electronic (UV/vis) spectra for group 11 MPACs exhibit the typical[5,16,17] metal cluster surface plasmon (SP) band[20] atop an absorbance decreasing monotonically from high to low energy that arises from electron−hole interactions.

† University of North Carolina.
‡ Iowa State University.
§ Oak Ridge Institute for Science and Education.
(1) (a) Belloni, J. *Curr. Opin. Colloid Interface Sci.* **1996**, *2*, 184. (b) Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457.
(2) Harikumar, K. R.; Ghosh, S.; Rao, C. N. R. *J. Phys. Chem. B* **1997,** *101***,** 536.
(3) Schmidt, T. J.; Noeske, M.; Gasteiger, H. A.; Behm, R. J.; Britz, P.; Brijoux, W.; Bönnemann, H. *Langmuir* **1997**, *13*, 2591.
(4) Sangregorio, C.; Galeotti, M.; Bardi, U.; Baglioni, P. *Langmuir* **1996**, *12*, 5800.
(5) Sinzig, J.; Radtke, U.; Quinten, M.; Kreibig, U. *Z. Phys. D* **1993**, *26*, 242.
(6) Toshima, N.; Harada, M.; Yamazaki, Y.; Asakura, K. *J. Phys. Chem.* **1992**, *96*, 9927.
(7) (a) Michaelis, M.; Henglein, A.; Mulvaney, P. *J. Phys. Chem.* **1994**, *98*, 6212. (b) Henglein, A.; Brancewicz, C. *Chem. Mater.* **1997**, *9*, 2164.
(8) Remita, S.; Mostafavi, M.; Delcourt, M. O. *Radiat. Phys. Chem.* **1996**, *47*, 275.
(9) Liz-Marzán, L. M.; Philipse, A. P. *J. Phys. Chem.* **1995**, *99*, 15120.
(10) Remita, H.; Khatouri, J.; Treguer, M.; Amblard, J.; Belloni, J. *Zeit. Phys. D* **1997**, *40*, 127.
(11) Schmid, G.; West, H.; Mehles, H.; Lehnert, A. *Inorg. Chem.* **1997**, *36*, 891.
(12) Nashner, M. S.; Frenkel, A. I.; Adler, D. L.; Shapley, J. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 7760.
(13) Hostetler, M. J.; Green, S. J.; Stokes, J. J.; Murray, R. W. *J. Am. Chem. Soc*. **1996**, *118*, 4212−4213.
(14) Brust, M.; Walker, M.; Bethell, D.; Schriffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801−802.
(15) Collier, C. P.; Saykally, R. J.; Shiang, J. J.; Henrichs, S. E.; Heath, J. R. *Science* **1997**, *277*, 1978.
(16) (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) Cleveland, C. L.; Landman, U.; Shafigullin, M. N.; Stephens, P. W.; Whetten, R. L. *Z. Phys. D* **1997**, *40*, 503. (c) Ingram, R. J.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Whetten, R. L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. *J. Am. Chem. Soc.* **1997**, *119*, 9279. (d) Schaaff, T. G.; Whetten, R. W. Private communication.
(17) (a) Schmid, G. *Clusters and Colloids. From Theory to Applications*; VCH: New York, 1994. (b) Haberland, H., Ed.; *Clusters of Atoms and Molecules*; Springer-Verlag: New York, 1994. (c) Hostetler, M. J.; Murray, R. W. *Curr. Opin. Colloid Interface Sci.* 1997, *2*, 42−49.

(18) It is conceivable that the bimodal core size distribution reflects a minor population of mono-metal nanoparticles, but the effect was only observed in one of five TEM images.
(19) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry,* 5th ed.; Wiley: New York, 1988.

Table 1.   Properties of Monolayer-Protected Alloy Clusters (MPACs)

metal salt ratio[a]	final cluster metal ratio	diameter (nm)	dec. temp (K)[b]	XPS S2p peak ratio[c]
Au:Ag (4:1)	1:0.4[d]	3.2[f]	531	1:2.8 (Au:Ag)
Au:Ag (2:1)	1:0.9[d]	3.2[f]	543	1:2.2 (Au:Ag)
Au:Ag (1:1)	1:1.4[d]	3.23 ± 0.8[e]	- - -	1:6.6 (Au:Ag)
Au:Ag (1:2)	1:1.6[d]	3.2[f]	544	1:5.2 (Au:Ag)
Au:Ag (1:4)	1:2.5[g]	3.2[f]	550	1:6.0 (Au:Ag)
Au:Cu (1:1)	1:1[g]	2.27 ± 0.39[e]	523	1:3.7 (Au:Cu)
Au:Ag:Cu (1:1:1)	1:0.9:0.4[g]	2.3[f]	530	1:5.5 (ca. Au:Ag)
Au:Pt (1:1)	1:0.3[d]	2.03 ± 0.39[e]	526	1:1.9[h]
Au:Pd (1:1)	1:3.9[d]	1.74 ± 0.35[e]	541	1:6.2[h]
Au:Ag:Cu:Pd (1:1:1:1)	1:1:0.1:3[d]	1.7[f]	535	1:0.2[h]

[a] $HAuCl_4 \cdot xH_2O$; $AgNO_3$; $Cu(NO_3)_2$; $H_2PtCl_6 \cdot xH_2O$; $\cdot K_2PdCl_4$. [b] Temperature at which 5% weight loss occurred by evolution of volatile disulfide; comparable values for mono-metal MPCs are 519 K (Au) and 540 K (Ag). [c] Ratio of the integrated area of the higher BE S2p doublet to the lower BE S2p doublet. [d] From band intensities of metal XPS. [e] Predominantly from TEM data. [f] From thermogravimetry, XPS and ^1H NMR line broadening data, as in ref 16a. [g] From elemental analysis. [h] The metal identity of each doublet could not be determined with confidence.
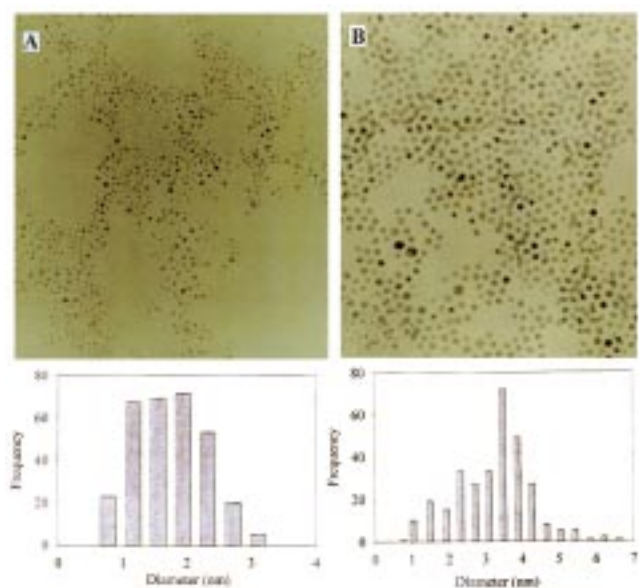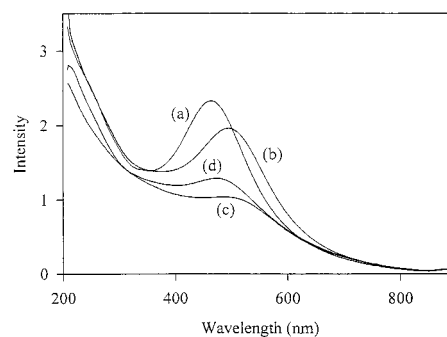

Figure 1. Transmission electron micrographs (insets are histograms) of the dodecanethiolate-protected (a) AuPd alloy MPAC and (b) AuAg alloy MPAC. TEM scale is 0.28 mm/nm.

Figure 2. UV/Vis spectra of dodecanethiolate-protected group 11 alloy clusters: (a) $AuAg_{2.5}$ (468 nm), (b) $AuAg_{1.4}$ (504 nm), (c) $AuAg_{0.4}$ (518 nm), and (d) $AuAg_{0.9}Cu_{0.4}$ (488 nm).

The SP band energy (and resulting solution color) proves to be quite sensitive to the MPAC core composition. That for Au/Ag MPACs, for example, varies smoothly with the metal ratio (Figure 2a−c) between the energies for mono-metal Ag (420 nm) and Au (520 nm) MPCs.[21] This spectral behavior rules out any substantial formation of mono-metal MPCs (and core−shell structures), since no MPAC preparation gave spectra with multiple SP bands. Interestingly, the presence of a group 10 metal in the MPAC suppresses SP bands of group 11 metals, an observation which has been interpreted for other nanoparticles to indicate[2−9] segregation of group 10 metals to the nanoparticle surface.

MPAC ^1H NMR spectral line widths are also sensitive to the identity of the metal core. The group 11 MPACs give broadened spectra similar to that of Au mono-metal clusters.[16a] However, inclusion of group 10 metals in the MPAC significantly reduces spectral line widths,[22] so that even the α-CH_2 (adjacent to the thiolate) resonance can be seen as two distinct triplets at 3.03

and 2.80 ppm (ratio of ca. 1 to 0.8, respectively). Similar peak splitting in the ^{13}C NMR spectra of very small Au mono-metal clusters has been attributed[16d] to differences between thiolate groups bound to core vertexes versus edge versus terrace-like sites. Further study of monolayer chemical shifts should supplement the presently limited experimental information available about the core shape.

In conclusion, thermal, optical, and electronic properties of MPACs can be systemically altered, and their core metals are partly segregated. Further MPAC chemical properties will be described in future reports.

Supporting Information Available: Details of sample preparation, XPS data (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA981454N

(20) Kreibig, U., Vollmer, M., Eds.; *Optical Properties of Metal Clusters*; Springer-Verlag: New York, 1995.
(21) Interpretation of band intensity data is complicated by other factors, such as core size effects.
(22) The origin of the line width change, including possible electronic effects of the core, is unclear. The ^1H resonances of group 10/11 MPACs are still much broader than those for typical small molecules, at least in part because of the MPACs' considerable rotational time constant.[16a]