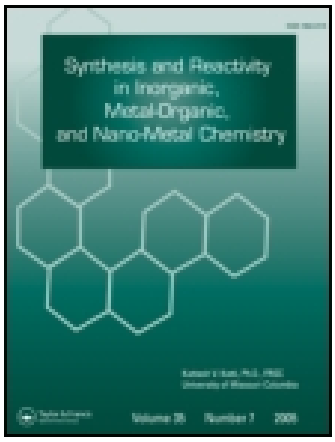
This article was downloaded by: [York University Libraries]
On: 28 December 2014, At: 13:23
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Zintl Polyanions as Metal Nano Particle Precursors

S. M. Lake [a] & J. J. Lagowski [a]
[a] Department of Chemistry and Biochemistry , The University of Texas at Austin , Austin, Texas, USA
Published online: 17 Feb 2007.

To cite this article: S. M. Lake & J. J. Lagowski (2006) Zintl Polyanions as Metal Nano Particle Precursors, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 36:6, 465-467

To link to this article: http://dx.doi.org/10.1080/15533170600777903

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry, 36:465–467, 2006
Copyright © 2006 Taylor & Francis Group, LLC
ISSN: 0094-5714 print / 1532-2440 online
DOI: 10.1080/15533170600777903

Taylor & Francis
Taylor & Francis Group

Zintl Polyanions as Metal Nano Particle Precursors

S. M. Lake and J. J. Lagowski
Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas, USA

Downloaded by [York University Libraries] at 13:23 28 December 2014

Bismuth nanoparticles have been produced by the oxidation of the Zintl polyanion Bi_4^{2-} in ethylenediamine solutions. TEM images indicate that the crystalline nanoparticles produced in the presence of polyethylene glycol are in the size range of ~20 nm. The oxidation of the polyanion by 2-octanol produce larger nanoparticles of bismuth (~50 nm).

Keywords Bismuth, nanoparticles, metal anions, non-aqueous solvents, synthesis

INTRODUCTION

Nanophase substances often exhibit different properties than those of the same substance in the bulk crystalline phase. Many of the new properties of nanophase materials (1–100 nm) arise because the critical length scales of physical phenomena become comparable or larger than the size of the nanoparticles.[1] In general, the synthesis of nanophase substances have involved the dispersion of bulk phases by physical processes, or most commonly, the use of chemical processes that start with conventional, molecular-sized species to produce solids in a chemical environment that ensures the dispersion of the desired products as nano-sized particles. By far, the favored method of producing nanophase substances involves the use of chemical processes that, as a group, possess a potential richness that allows for the possibilities of chemical manipulation to produce nanophase substances with well-defined properties.

We report here the results of preliminary experiments designed to produce *metal* nanoparticles. The work reported here is the latest manifestation of our long-time interest in metal anions, a species that can be stabilized in non-aqueous solvents such as amines and ethers.[2–11] Not surprisingly, metal anions are highly reducing species, the chemical characteristic that is the basis for the production of metal nanoparticles.

$$M^{n-} + [OX] \longrightarrow M_{x(s)} + [OX^{n-}]$$

We have chosen the well-characterized B_4^{2-} polyanion[12] for these initial experiments. The polyanion is produced from the extration of a Na:Bi alloy by ethylenediamine.[12–13]

EXPERIMENTAL

All reactions were performed in an anaerobic environment because H_2O, O_2, and CO_2 can be reduced by metal anions. Ethylenediamene was purified by the method of Dye.[14] Bismuth-sodium alloys (1 : 1 molar ratio) were prepared in vacuo by melting the appropriate quantities of the constituent metals. The alloy was equilibrated with the dry ethylenediamine solvent producing a red-brown colored solution, aloquots of which were treated with an oxidant to yield the desired nanoparticles. The products were characterized by TEM and elemental analysis using X-ray fluorescence techniques.

RESULTS AND DISCUSSION

Two (2) different oxidizing environments were investigated; (**I**) isopropyl alcohol in the presence of the surfactant, polyethylene glycol (PEG), and (**II**) 2-octanol. Both environments produced particles of bismuth metal. The results of these experiments follow.

I. A TEM photograph (Figure 1) of the product formed by the oxidation of Bi_4^{2-} in the presence of PEG consists of nanoparticles in the range of ~20 nm. The crystalinity of the nanoparticles produced in environment **I** is established by the TEM data shown in Figure 2, from which data we extracted a lattice spacing of ~0.33 nm.

II. In this environment, where 2-octanol is the oxidant, we assume that the alcohol (or its anion) can also act as a surfactant. The TEM of the product formed in this environment (Figure 3) consists of nanoparticles of bismuth in the ~50 nm size. The larger sized nanoparticles produced in environment **II** compared with those produced in environment

Received 23 February 2006; accepted 1 April 2006.
Address correspondence to J. J. Lagowski, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712, USA. E-mail: jjl@mail.utexas.edu

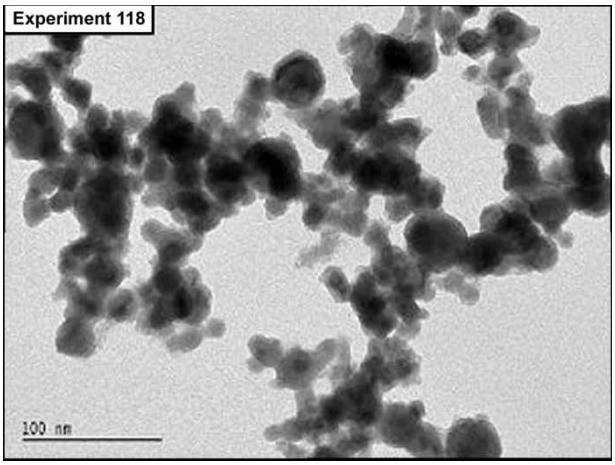


FIG. 1. TEM photograph of the product formed by the oxidation of Bi_4^{2-} by PEG.

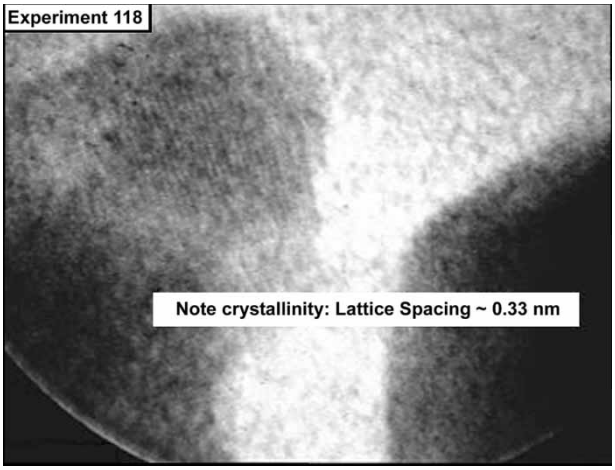


FIG. 2. TEM data indicating crystallinity of the Bi nanoparticles characterized in Figure 1.

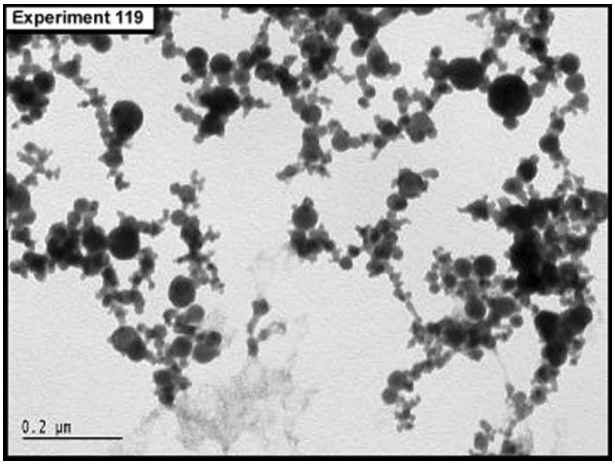


FIG. 3. TEM photograph of the product formed by the oxidation of Bi_4^{2-} by 2-octanol.

I, most probably arises from the fact that PEG is a more effective surfactant than 2-octanol; however, this is only a conjecture that needs further investigation. Clearly, our approach to the generation of bismuth (and probably other elements) is viable and needs further investigation. The access to nanophase bismuth materials has been limited to (a) the formation of very dilute stable colloids,[15] (b) an in situ polymerization process,[16] and (c) by the use of reverse micells.[17] The nanoparticles produced in (a) were formed in very low concentrations and were determined to be 8–12 nm in size. Those produced via (b) were 20 nm in size; and those produced by (c) were "less than 10 nm" in size.

We continue to investigate the formation of metal nanoparticles using homonuclear as well as heteronuclear Zintl anions.

ACKNOWLEDGEMENT

We gratefully acknowledge the support of this research by the Robert A. Welch Foundation of Jouston, Texas.

REFERENCES

1. Lue, J. T. A review of characterization and physical property studies of metallic nanoparticles. *J. Phys. Chem. Solids* **2001**, *62*, 1599–1612.
2. Bratsch, S. G.; Lagowski, J. J. On the existence of Na^- in liquid ammonia. *J. Phys. Chem.* **1984**, *88*, 1086–1089.
3. Pawlak, Z.; Lagowski, J. J. Gold (Au^-) and Silver (Ag^-) anions in liquid ammonia. *Electrocatal., Mater. Symp. Electrochem. Sect. Pol. Chem. Soc.* **1988**, *9*, 248–255.
4. Peer, W. J.; Lagowski, J. J. Metal ammonia solutions. XI. Au^-, a solvated transition metal anion. *J. Am. Chem. Soc.* **1978**, *100*, 6260–6261.
5. Peer, W. J.; Lagowski, J. J. Metal-ammonia solutions. XIII. solutions of lanthanoid metals. *J. Phys. Chem.* **1980**, *84*, 1110–1119.
6. Montes, L.; Lagowski, J. J. Electrochemical behavior of sodium anions. *J. Phys. Chem. B.* **2003**, *107* (38), 10665–10670.
7. Teherani, T. H.; Peer, W. J.; Bard, A. J.; Lagowski, J. J. Anodic electrodeposition of gold from liquid ammonia solutions. *J. Electrochem. Soc.* **1978a**, *125*, 1717–1718.
8. Teherani, T. H.; Peer, W. J.; Bard, A. J.; Lagowski, J. J. Electrochemical behavior and standard potential of Au^- in liquid ammonia. *J. Am. Chem. Soc.* **1978b**, *100*, 7768–7769.
9. Tran, N. E.; Lagowski, J. J. Metal ammonia solutions: Solutions containing argentide ions. *Inorganic Chem.* **2001**, *40* (5), 1067–1068.
10. Chlistunoff, J. B.; Lagowski, J. J. Cathodic generation and oxidation of lead zintl ion Pb_9^{4-} in potassium iodide solutions in liquid ammonia. *J. Phys. Chem. B* **1997**, *101*, 2867–2873.
11. Chlistunoff, J. B.; Lagowski, J. J. Surface alloying of lead as a step in the cathodic generation of the Pb_9^{4-} in Kl and RbBr liquid ammonia solutions. *J. Phys. Chem. B* **1998**, *102*, 5800–5809.
12. Lake, S. M. *The Cathodic Generation of Zintl Anions in Amines: Electrochemistry of Bismuth Polyanions in Liquid Ammonia*. Ph.D. Dissertation, The University of Texas at Austin, 1999.

Downloaded by [York University Libraries] at 13:23 28 December 2014

13. Warren, C. J.; Haushalter, R. C.; Bocarsley, A. B. The electrochemical synthesis of telluride Zintl anions. *J. Alloys Cmpds.* **1995**, *229*, 175–205.
14. Dye, J. L. Electrides, negatively charged metal ions, and related phenomena. *Prog. Inorg. Chem.* **1984**, *32*, 327.
15. Gutierrez, M.; Henglein, A. Nanometer-sized bi particles in aqueous solution: Absorption spectrum and some chemical properties. *J. Phys. Chem.* **1996**, *100*, 7656–7661.
16. Fang, J.; Stokes, K. L.; Wiemann, J.; Zhou, W. Nanocrystalline bismuth synthesized via an in situ polymerization-microemulsion process. *Mater. Lett.* **2000**, *42*, 113–120.
17. Foos, E. E.; Stroud, R. M.; Berry, A. D.; Snow, A. W.; Armistead, J. P. Synthesis of nanocrystalline bismuth in reverse micelles. *J. Am Chem. Soc.* **2000**, *122*, 7114–7115.

Downloaded by [York University Libraries] at 13:23 28 December 2014