

# Preparation of a wide array of ultra-high purity metals, metal oxides, and mixed metal oxides with uniform particle sizes from 1 nm to bulk

S. Liu, Q. Liu, S. Smith, J. Boerio-Goates, and B. Woodfield\*

\*Brigham Young University, Provo, UT, USA. [Brian\\_Woodfield@chem.byu.edu](mailto:Brian_Woodfield@chem.byu.edu)

## ABSTRACT

In this paper we discuss the materials that can now be produced using a novel (and still proprietary) method for producing high-purity metal, metal oxide, and mixed-metal oxide particles. The particles formed are uniform in size with dimensions that can range from 1 nm to greater than 10  $\mu\text{m}$ . The metal oxides produced by this method include (but are not limited to) the transition metals, rare earth metals, and the Groups I, II, and III metals of the Periodic Table. Mixed-metal oxides of any combination of the aforementioned metals with any stoichiometry can also be produced. Additionally, the final oxidation state of the metal can be controlled. The present method is unique and advantageous because it uses a simple process to prepare large quantities of a vast array of metal oxides, mixed metal oxides, and metals with purity levels as high as 99.999+% with tight control of the particle size ( $\pm 10\%$ ). This method is also much lower in cost and more environmentally benign than other techniques currently available.

**Keywords:** synthesis, nanoparticles, metals, metal oxides, mixed metal oxides

## 1 INTRODUCTION

Nanomaterials possess unique and useful chemical, physical, and mechanical properties, and they can be used in a wide range of industrial, biomedical, and electronic applications [1-3]. Exploration of the properties and uses for nanoscale metal oxides, metals, and alloys is underway in a variety of disciplines such as chemistry, physics, materials science, and engineering. The importance of such new interdisciplinary investigations may be realized in the design and characterization of advanced materials. Studies of nanometer-sized metal oxides, mixed-metal oxides, metals, and alloys provide powerful examples of how material performance can be optimized by controlling particle size.

The metal oxides, including mixed-metal oxides, especially those containing transition metals, encompass a wide range of technologically important materials ranging from gas sensors, catalytic supports, optical coatings, electrodes in batteries, and catalysts to gate dielectrics in the semiconductor industry [4-5]. In all of these roles, the

surface or interfaces of the oxide dominates the activity. Because of their greater percentage of surface area, nanocrystalline metal oxides are often much more reactive than their conventional or bulk metal oxide counterparts. Considerable effort has already been focused on the synthesis and use of transition metal oxides at the nanoscale [6-8]. For example, zinc oxide nanoparticles are useful in the rubber industry in the areas of activation, acceleration, biochemical activity, dielectric strength, heat stabilization, latex gelatin, light stabilization, pigmentation, reinforcement, rubber-metal bonding, and tack retention. Also, ZnO nanoparticles can be greatly modified in their optical properties to increase the absorption of light in the visible region, a process known as sensitization, which is generally carried out by addition of certain dyes that are absorbed on the surface of ZnO nanoparticles [9-11].

Nanocrystalline metal oxides, including mixed-metal oxides, of elements in the rare earth block also play a vital role in many areas of chemistry and physics. Ceria (cerium oxide), for instance, has been recently used for applications requiring ionic conductivity at low temperatures, such as the manufacture of solid oxide fuel cells and other electrochemical applications [12]. An important property required to use these materials in such applications is nano-crystallinity, that is, to have crystalline particles whose dimensions are in the range of 5 to 100 nm.

Nanometer metals and alloys [13-16] have been extensively used as structural materials in such high performance components as medical implants and aerospace components; they can also be used as catalysts, corrosion-resistant coatings, and permanent magnets. The economic impact of these materials is as unappreciated as the diversity of their applications. For example, the alloys constitute a very important class of materials for electromagnetic applications, such as: (1) magnetic, magnetoresistive, and magnetostrictive applications; (2) superconductor applications, the most powerful superconducting magnets are built with  $\text{Nb}_3\text{Sn}$ ; (3) semiconductor and optical applications, alloys are indispensable for optoelectronic devices such as optical switches, diffraction gratings, filters, solar cells, photodetectors, light emitting diodes, and lasers; (4) magneto-optical applications; and (5) thermoelectric applications.

Techniques for producing nanocrystalline materials fall into one of three general categories [17-19], namely, mechanical processing (milling), chemical processing (precipitation), or thermal processing (evaporation and condensation). It is beyond the scope of this paper to provide a thorough review of existing synthetic techniques. However, conventional techniques for nanoparticle production have been plagued by drawbacks in (a) the formation of uniformly sized and high-purity nanoparticle products, (b) easily producing particles sizes of less than 10 nm, (c) controlling surface morphologies, (d) producing large or even industrial scale quantities, and (e) the high cost (time, specialized equipment, and materials) of production. Additionally, synthetic techniques developed for one metal or mixed-metal oxide often do not transfer to other important nano-oxides. New methods are needed that overcome these problems, enabling the synthesis of a wide range of nano-oxide materials in large quantities using a single transferable technique. Also needed are new and reliable metal oxide nanoparticle products with improved characteristics and properties for use in diverse applications.

## 2 EXPERIMENTAL

We have recently developed a truly unique and transferable method for producing large quantities of nanometer metal or mixed-metal oxide powders with ultra-high purities and with tight control of the particle size from amorphous to bulk, as well as for producing nanometer metal and metal alloy powders. In general terms, the technique consists of mixing metal-containing starting materials in appropriate stoichiometric ratios to form a novel precursor material, which is later heated to form the nanomaterial product. Details on the actual procedures and reactants will be reported elsewhere. The purpose of this paper is to provide a description of the range of materials that can now be produced and a demonstration of some of their unique properties. Knowledge of the availability of these types of materials is important for those developing new applications. To this end, a summary of the materials that can be produced, the advantages, and unique features of these new nanoparticles and the synthetic method are given below:

1. Practically *all* metal oxides in the transition, rare earth, and group III, IV, etc. blocks can be produced with well controlled particle sizes from 1 nm to bulk.
2. An innumerable array of mixed-metal oxides of any combination of metals (including group I and group II) and stoichiometric ratios with controlled particle sizes from 1 nm to bulk can also be produced. Not only does this open up the ability to produce, for the first time, a vast assortment of nano-sized mixed metal oxides, but this also provides a new synthetic pathway to produce novel metal oxide combinations.
3. The size distribution of the particles is very tight with typical distributions of less than 10%.

4. The chemical purity can be as high as 99.999+% and is only dependent on the purity of the starting materials. Surface morphologies are uniform, surfaces are contaminant-free, the surface water is minimized, and the particles are crystalline. Indeed, the powders produced with this method are free-flowing and minimally agglomerated.
5. The oxidation state of the product can also be controlled to produce high oxidation state oxides (such as  $\text{Co}_3\text{O}_4$ ), low oxidation state oxides (such as  $\text{CoO}$ ), and even nano metals and metal alloys.
6. The process is green and produces no solid or liquid waste products.
7. Industrial scale quantities of high purity product can be produced in less than 3 hours. By hand a hundred grams of product can be made in that 3-hour window. With automation, it will be a simple matter to produce kilograms of product.
8. The cost of the product is essentially the cost of the starting materials. No exotic or expensive equipment (plasmas, lasers, vacuums, etc.) are required.

## 3 RESULTS

Shown in Table 1 is a representative list of materials and their resulting particle sizes that we have synthesized using our new synthetic method.

| Material   | Size (nm)             |
|--|-----------------------|
| CoO  | $8 \pm 1$             |
| $\text{Co}_3\text{O}_4$  | $8 \pm 1$             |
| NiO  | $3 \pm 0.5, 9 \pm 1$  |
| CuO  | $8 \pm 1$             |
| ZnO  | $8 \pm 1, 16 \pm 1$   |
| $\text{Fe}_2\text{O}_3$  | $12 \pm 1$            |
| $\text{Fe}_3\text{O}_4$  | $10 \pm 1$            |
| $\text{LiCoO}_2$   | $10 \pm 1$            |
| $\text{In}_2\text{O}_3$  | $8 \pm 1$             |
| $\text{SnO}_2$   | $12 \pm 1$            |
| $\text{Al}_2\text{O}_3$  | $2 \pm 0.5, 8 \pm 1$  |
| $\text{NiFe}_2\text{O}_4$  | $7 \pm 1$             |
| $\text{Zn}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$                      | $8 \pm 1$             |
| $\text{Li}_{0.15}\text{Zn}_{0.3}\text{Ni}_{0.4}\text{Fe}_{2.15}\text{O}_4$ | $8 \pm 1$             |
| $\text{Y}_2\text{O}_3$   | $1 \pm 0.5, 13 \pm 1$ |
| $\text{Nd}_2\text{O}_3$  | $9 \pm 1$             |
| $\text{Ag}_2\text{O}$  | 65                    |
| Ni   | 40                    |
| $\text{TiO}_2$   | 7                     |
| $\text{ZrO}_2$   | 5                     |
| $(\text{Y})\text{ZrO}_2$   | 7                     |
| $\text{Bi}_2\text{O}_3$  | 10                    |
| Ni, Co alloys  | 40 - 70               |

**Table 1:** Representative examples of materials and the resulting particle sizes synthesized with our new generalized methodology.

As is clearly evident, the range of materials that can be produced using a single methodology is remarkable including transition metal oxides, semi-metal oxides, rare earth oxides, mixed-metal oxides, Li-doped oxides, and nano metals.

We have performed careful characterizations on many of these samples and can show that these materials are phase pure, chemically pure, have a uniform particle size, and maintain their physical properties. For example, shown in Figure 1a is the powder x-ray diffraction (XRD) for CoO collected with a scan rate of 0.2 2 $\theta$ /min. As can be seen, the CoO product is phase pure even using the slowest scan rate of the diffractometer. The average particle size of 8 nm was calculated using the Scherrer formula from the peak width at half maximum for the principle XRD peak. Shown in Figure 2a is a transmission electron micrograph (TEM) of the CoO sample where the size uniformity is evident and the particle size is consistent with the average size calculated from the XRD data.

Further characterizations of the CoO sample were performed using inductively coupled plasma (ICP) to check for chemical impurities. The ICP results showed the chemical impurities to be less than 10 ppm. The water content of the CoO sample was measured by thermogravimetric analysis (TGA). A sample of CoO was heated under an atmosphere of He gas and the mass change was measured. From these measurements, the water content was calculated to be 2.23%. This same sample of CoO was heated again but in a reducing atmosphere (5% H<sub>2</sub> gas) and to high temperatures. The resulting mass change was due solely to the reduction of CoO to Co metal from which the oxygen content could be calculated. The combined oxygen and water content measurements allowed us to determine the molecular formula of the CoO sample to be CoO<sub>1.006</sub>·0.095H<sub>2</sub>O. Notice that the water content for these materials is extremely low.

In order to further characterize the physical properties of the CoO sample, we have also measured the specific heat of the sample in the region of the antiferromagnetic transition and compared the results to previous measurements on a high-purity single crystal, a 60  $\mu$ m powder sample, and a previous 7 nm sample that had typical levels of phase and chemical impurities for a sample produced by precipitation. Shown in Figure 3 is a comparison of the specific heat results for the various samples. Note for the single crystal, the antiferromagnetic transition is sharp and high, the 60  $\mu$ m sample still has a sharp transition that is not as high as the single crystal transition (as expected), and the 7 nm sample has an identifiable transition that is broad and at a lower temperature. What is surprising is that the specific heat results for our 8 nm CoO sample, while lower than the 60  $\mu$ m powder data, are still sharp and well defined and are similar in shape to the 60  $\mu$ m powder data. These results show that the CoO sample produced using our technique must be highly crystalline and, consequently, maintains its magnetic properties even at the nanoscale.

Shown in Figures 1b, 1c, and 1d are further examples of XRD data for other samples produced by our technique, and shown in Figure 2b, 2c, and 2d are further examples of TEM images. Important points that should be noted include (a) the phase purity of the samples as shown in the XRD data, (b) the uniform particle sizes as shown by the TEM images, (c) the well-defined and small size of the NiO sample, and (d) the Y<sub>2</sub>O<sub>3</sub> particles shaped as rods and with clearly defined fringe patterns that provide further support for the highly crystalline nature of our particles.

Figure 1: X-ray powder diffraction data for (a) CoO, (b) NiO, (c) NiFe<sub>2</sub>O<sub>4</sub>, and Li<sub>0.15</sub>Zn<sub>0.3</sub>Ni<sub>0.4</sub>Fe<sub>2.15</sub>O<sub>4</sub>. Particle sizes were calculated using the Scherrer formula using the most intense peak.

Figure 1a: XRD of CoO

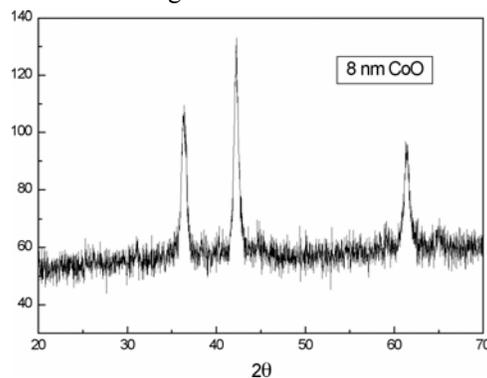


Figure 1b: XRD of NiO

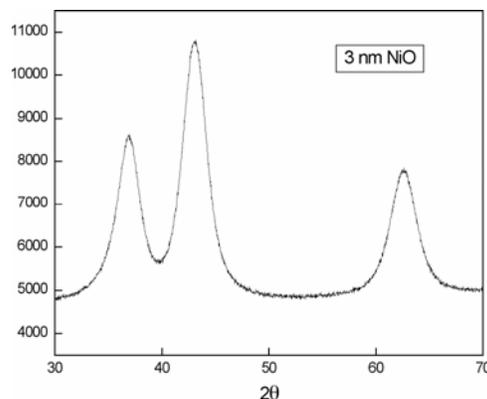


Figure 1c: XRD of NiFe<sub>2</sub>O<sub>4</sub>

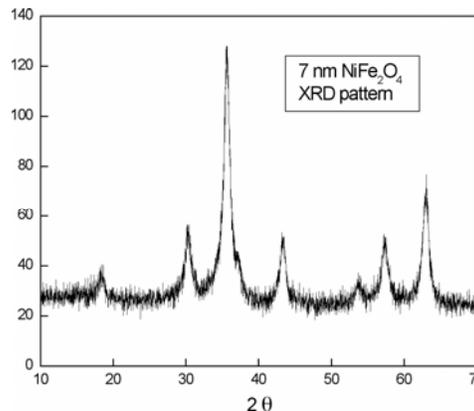


Figure 1d: XRD of  $\text{Li}_{0.15}\text{Zn}_{0.3}\text{Ni}_{0.4}\text{Fe}_{2.15}\text{O}_4$

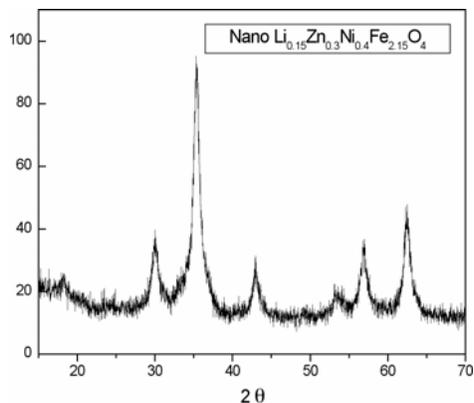


Figure 2: Transmission electron microscopy images of for (a) CoO, (b) NiO, (c)  $\text{NiFe}_2\text{O}_4$ , and (d)  $\text{Y}_2\text{O}_3$ . Notice that the  $\text{Y}_2\text{O}_3$  forms as rods and highly crystalline nature of the particles as evidenced by lattice patterns.

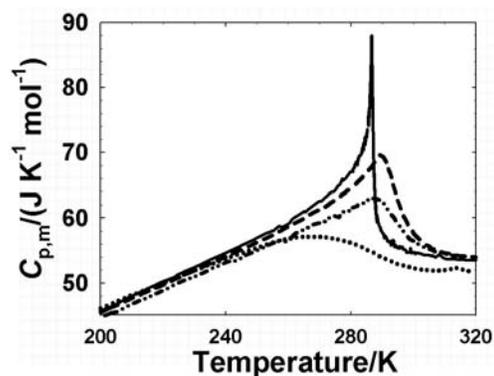
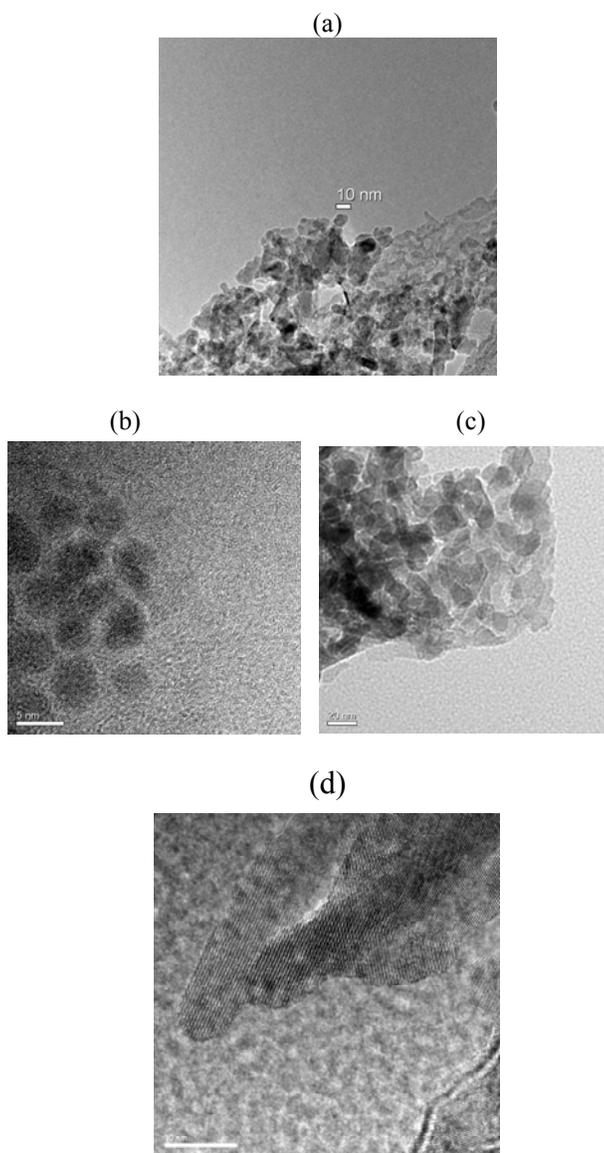


Figure 3: Specific heat of various CoO samples including a high-purity annealed single crystal ( $\square$ ), a 60  $\mu\text{m}$  powder (- - -), a 7 nm CoO of poor quality ( $\bullet\bullet$ ), and an 8 nm CoO sample produced using our technique ( $\bullet-$ ).

## REFERENCES

- [1] M. Gell, *Mater. Sci. Eng. A204* 1-2, 246 (1995).
- [2] C.C. Koch, *Nanostruct. Mater.* 2(2), 109 (1993).
- [3] H. Gleiter, *Nanostruct. Mater.* 1(1), 1-20 (1992).
- [4] F.T. Quinlan, R. Vidu, L. Predoana, M. Zaharescu, M. Gartner, J. Griza, P. Stroeve, *Ind. Eng. Chem. Res.* 43, 2468 (2004).
- [5] A. Szatvanyi, M. Crisan, D. Crisan, A. Jitianu, L. Stanciu, M. Zaharescu, *Rev. Rom. Chim.* 47(12), 1255 (2002).
- [6] G.F. Gaertner, P.F. Miquel, *Nanostruct. Mater.* 4(3), 559-568 (1993).
- [7] J.L. Katz, P.F. Miquel, *Nanostruct. Mater.* 4(5), 551-557 (1994).
- [8] B. Gunther, A. Kumpmann, *Nanostruct. Mater.* 1(1), 27-30 (1992).
- [9] S. Pillai, J. Kelly, D. McCormack, R. Ramesh, *J. of Mater. Chem.* 14, 1572 (2004).
- [10] D.W. Bahnemann, C. Kormann, M.R. Hoffmann, *J. Phys. Chem.* 91, 789 (1987).
- [11] E. A. Meulenkamp, *J. Phys. Chem. B*, 102, 5566 (1998).
- [12] G. Balazs, R. Glass, *Solid State Ionics* 76, 155 (1995).
- [13] K.S. Suslick, S.B. Choe, A.A. Cichoulus, M.W. Grinstaff, *Nature* 353, 414 (1991).
- [14] K.S. Suslick, T. Hyeon, M. Fang, *Chem. Mater.* 8, 2172 (1996).
- [15] X. Cao, Y. Koltypin, R. Prozorov, G. Kataby, A. Gedanken, *J. Mater. Res.* 12, 402 (1997).
- [16] K.V.P.M. Shafi, A. Gedanken, R. Goldfarb, I. Felner, Y. Koltypin, *J. Appl. Phys.* 81, 6901 (1997).
- [17] C.C. Koch, *Nanostruct. Mater.* 2(2), 109 (1993).
- [18] B. Gunther, A. Kumpmann, *Nanostruct. Mater.* 1(1), 27 (1992).
- [19] Y. Mizoguchi, M. Kagawa, M. Suzuki, Y. Syono, T. Hirai, *Nanostruct. Mater.* 4(5), 591 (1994).