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LETTERS

Synthesis of Nanoscale Metal Oxide Particles Using Laser Vaporization/Condensation in a Diffusion Cloud Chamber

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A novel method which combines laser vaporization of metals with controlled condensation in a diffusion cloud chamber is used to synthesize nanoscale metal oxide and carbide particles (10-20 nm) of homogeneous size and well-defined composition. The following oxides have been synthesized: ZnO, SiO₂, Fe₂O₃, Bi₂O₃, PdO, NiO, AgO, TeO, Sb₂O₃, TiO₂, ZrO₂, Al₂O₃, CuO, In₂O₃, SnO, V₂O₅, and MgO. The microscale structures of the SiO₂ and Al₂O₃ particles exhibit secondary open-structure arrays of interesting weblike matrices with significant volumes of voids in the aggregate structure. These materials may have special applications in catalysis and as reinforcing agents for liquid polymers.

Introduction

The synthesis of nanoscale particles has received considerable attention in view of the potential for new materials with novel properties and the design of catalysts with specific dimensions and compositions.¹⁻⁴ Nanoscale particles possess several unique properties such as large surface areas, unusual adsorptive properties, surface defects, and fast diffusivities. The characterization of these properties can ultimately lead to identifying many potential uses, particularly in the field of catalysis. For example, particles of metal oxides and mixed oxides such as SiO₂/TiO₂ exhibit unusual acidic properties and can be used as acidic catalysts.⁵

A wide range of scientifically interesting and technologically important nanoparticles has been produced by both chemical^{6,7} and physical⁸⁻¹¹ methods. The most common physical methods involve gas-condensation techniques where oven sources are usually used to produce metal vapors. Despite the success of this method, there are, however, some problems and limitations, such as possible reactions between metal vapors and oven materials, inhomogeneous heating which can limit the control of particle size and distribution, limited success with refractory metals due to low vapor pressures, and difficulties in controlling the in composition between the alloys and the mixed vapors. Laser vaporization techniques provide several advantages over other heating methods such as the production of high density vapor of any metal within an extremely short time $(10^{-8} s)$, the generation of a directional high-speed metal vapor from the solid target which can be useful for directional deposition of the particles, the control of the evaporation from specific spots on the target as well as the simultaneous or sequential evaporation of several different targets.¹² Some of these advantages have been demonstrated in the synthesis of ultrafine metal particles,¹³ but the control of the nucleation process which strongly affects the particles' size, composition, and morphology has not yet been fully achieved.

composition of the mixed metal particles due to the difference

The purpose of this letter is to describe a novel technique to synthesize nanoparticles of controlled size and composition. Our technique combines the advantages of pulsed laser vaporization with controlled condensation in a diffusion cloud chamber under well-defined conditions of temperature and pressure. The present report pertains specifically to the synthesis of metal oxides and mixtures of oxides. Subsequent publications will focus on other nanoparticles such as metal nitrides, carbides and different forms of metal-carbon particulates.

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Experimental Section

A modified upward thermal diffusion cloud chamber was used for the synthesis of the nanoscale particles. This chamber has been commonly used for the production of steady-state supersaturated vapors for the measurements of homogeneous and photoinduced nucleation rates of a variety of substances.¹⁴ A detailed description of the chamber and its major components can be found in several references.^{14,15} Here we offer only a very brief description of the modifications relevant to the synthesis of the nanoparticles. The chamber consists of two horizontal, circular stainless steel plates, separated by a circular glass ring. A metal target of interest sets on the lower plate, and the chamber is filled with a carrier gas such as He or Ar (99.99% pure) containing a known composition of the reactant gas (e.g., O₂ in case of oxides, N2 or NH3 for nitrides, CH4 or C2H4 for carbides, etc.). The metal target and the lower plate are maintained at a temperature higher than that of the upper one (temperatures are controlled by circulating fluids). The top plate can be cooled to less than 120 K by circulating liquid nitrogen. The large temperature gradient between the bottom and top plates results in a steady convection current which can be enhanced by using a heavy carrier gas such as Ar or Kr under high-pressure conditions (1-103 Torr).

The metal vapor is generated by pulsed laser vaporization using the second harmonic (532 nm) of a Nd:YAG laser (15-30 mJ/ pulse). Laser vaporization typically releases more than 1014 metal atoms/pulse (2 \times 10⁻⁸ s). The hot metal atoms react with O₂ (in the case of oxides syntheses) to form vapor-phase metal oxide molecules which undergo several collisions with the carrier gas, thus resulting in efficient cooling via collisional energy loss. Under the total pressure employed in the current experiments (800 Torr), it is expected that the metal atoms and the oxide molecules approach the thermal energy of the ambient gas within several hundred microns from the vaporization target. The unreacted metal atoms and the less volatile metal oxide molecules are carried by convection to the nucleation zone near the top plate of the chamber. As in the conventional chamber, the temperature profile is expected to be a linear function of elevation in the chamber. Since the equilibrium vapor pressure (P_e) is approximately an exponential function of temperature, the metal oxide vapor can easily be supersaturated (supersaturation S = P/Pe, where P is the actual partial pressure of the metal oxide in the chamber) in the nucleation zone near the top plate. This supersaturation can be made as large as desired by increasing the temperature gradient between the chamber plates. The higher the supersaturation, the smaller the size of the nucleus required for condensation.¹⁴ Therefore, by controlling the temperature gradient, the total pressure and the laser power (which determines the number density of the metal atoms released in the vapor phase), it is possible to control the size of the condensing particles. This is the basic principle of our method.

Nichrome heater wires are wrapped around the glass ring and provide sufficient heat to prevent condensation on the ring and to maintain a constant temperature gradient between the bottom and top plates. The particles formed in the nucleation zone are condensed on the top plate during the laser vaporization (typically running at 10 Hz for about 1-2 h), then the chamber is brought to room temperature, and the particles are collected under atmospheric conditions. No particles are found on any other place in the chamber except on the top plate. Glass slides or metal wafers can be attached to the top plate when it is desired to examine the morphology of as-deposited particles.

Results and Discussion

Figure 1 displays a SEM micrograph obtained for SiO₂ particles synthesized using 20% O₂ in He at a total pressure of 800 Torr and top and bottom plate temperatures of -100 and 20 °C, respectively. The particles exhibit a unique agglomerate pattern



Figure 1. SEM micrograph of SiO₂ particles.



Binding Energy (eV)

Figure 2. Ti(2p) XPS spectra of TiO₂ nanoparticles synthesized in O_2/Ar (upper spectrum) and in O_2/He (lower spectrum).

which appears as a weblike matrix. On the basis of the TEM analysis of the same sample, an individual particle's size is estimated between 10 and 20 nm, which suggests a range from several hundred to a few thousand molecules per particle. Decreasing the temperature gradient between the chamber plates results in larger particle sizes. The agglomerate pattern is quite different from other nanoparticles synthesized using conventional oven or sputtering sources.⁸⁻¹¹ The persistence of the web-type morphology appears to be related to the size and type of the particles. One feature offered by this structure is the potential for specific catalytic activity and for reinforcing agents for liquid polymers.

To illustrate the effect of the $O_2/carrier$ gas mixture on the ratio of the oxidized-to-nonoxidized metal particles, we measured the X-ray photoelectron spectra (XPS) of the particles prepared under different experimental conditions. Figure 2 illustrates the results for TiO₂ particles synthesized using O_2/Ar and O_2/He mixtures containing the same concentration of O_2 (20%). The XPS spectra show two small peaks at 456 and 462 eV which are due to the $2p_{3/2}$ and $2p_{1/2}$ core level of Ti metal. As expected for oxide formation, these peaks are shifted to 458 and 464 eV, respectively, in the TiO₂ particles. The TiO₂/Ti ratios in the samples synthesized in Ar and He are estimated as 65% and 94%, respectively. Therefore, it appears that more efficient oxidation takes place in He than in Ar, and this may be attributed to



Figure 3. (a) Raman spectra of TiO₂ nanoparticles synthesized in O₂/Ar mixture. Laser power: 40 mW at 5145 Å, slit width: 2 cm^{-1} . (b) Raman spectra of TiO₂ nanoparticles synthesized in O₂/Ar (upper spectrum) and in O₂/He (lower spectrum).

inefficient cooling of the hot metal atoms in He which could lead to higher reaction probability with O_2 . Furthermore, the diffusion coefficient of O_2 is greater in He than in Ar, and this is related to the efficiency of the oxidation process. It is also important to note that the oxide/metal ratio in the nanoparticles can be controlled by varying the O_2 concentration in a given carrier gas (He or Ar). In this way, nanoparticles containing more than 99% oxide molecules have been synthesized.

Figure 3 displays representative Raman spectra of TiO_2 nanoparticles prepared using Ar or He as a carrier gas. As shown in Figure 3a, the particles synthesized in Ar exhibit the characteristic Raman peaks of the nanoscale anatase phase of TiO_2 (the low temperature phase).^{16,17} The Raman line at 144 cm⁻¹ is the most intense line in the Raman spectrum of the anatase natural crystal,¹⁷ and this line is observed at 142 cm⁻¹ in the spectrum of the nanoparticles shown in Figure 3a. Other Raman lines of the anatase nanoparticles are observed near 396, 516, and 638 cm⁻¹ in good agreement with the corresponding lines reported for the bulk materials. For example, the major Raman lines observed for natural polycrystalline, for single crystal, and for synthetic powder of anatase TiO₂ are reported at (392, 510, 633 cm⁻¹), (400, 515, 640 cm⁻¹), and (393, 512, 635 cm⁻¹), respectively.¹⁷

Figure 3b compares the Raman spectra of the TiO_2 nanoparticles synthesized in He and in Ar and shows that the former particles exhibit Raman features characteristic of both the anatase and the rutile phases, thus indicating a mixture of the two forms. Previous Raman measurements on nanoscale TiO_2 particles showed that both the rutile and anatase phases were present in



Figure 4. Raman spectra of the nanoparticles synthesized by laser vaporization of Titanium in 20% ethylene/He mixture. Laser power: 400 mW at 4880 Å. Slit width: 2 cm⁻¹. Laser plasma lines (dotted regions) have been eliminated for clarity.

the sample with the rutile phase being the most dominant.¹⁸ It is well-known that the rutile phase can be obtained by hightemperature annealing of the anatase particles.¹⁶ This is consistent with the inefficient collisional cooling of He which may result in significant formation of the high-temperature rutile phase. However, it is remarkable that by using Ar as a carrier gas, it is possible to exclusively synthesize the anatase form of TiO₂.

To demonstrate the potential of our method for the synthesis of mixtures of nanoparticles of controlled composition, we prepared several homogeneous mixtures of oxides such as CuO/ZnO, TiO₂/Al₂O₃, and TiO₂/Al₂O₃/ZnO. In these experiments, laser vaporization is alternated on the different metal targets of interest, and by adjusting the number of laser shots on each target, we were able to control the composition of the oxides mixture. For example, in the case of CuO/ZnO mixtures, laser vaporization of Cu/Zn targets over successive duration of 1000 shots on each target, 1000 (Cu)/2000 (Zn), and 3000 (Cu)/1000 (Zn) resulted in intimate mixtures containing CuO/ZnO with the ratios 20/80, 6/94, and 48/52, respectively, as determined from the SEM analyses of the particles.

Finally, we demonstrate the potential for the synthesis of different nanoparticles other than oxides by reacting the metal atoms with other gases such as hydrocarbons, N₂, NH₃, or CO₂. Figure 4 displays the Raman spectrum obtained for the nanoparticles synthesized by laser vaporization of Ti in He carrier gas containing 20% ethylene. The three Raman peaks shown in Figure 4 appear in close proximity to the Raman lines characteristic of TiO₂ (Figure 3). Since the force constants of the Ti–O and Ti–C bonds are nearly similar, one expects small Raman shifts between Ti–O and Ti–C bonds. This suggests that the nanoparticles may contain species involving Ti–C or TiC₂ bonds. Laser desorption mass spectrometry¹⁹ of the same sample shows peaks corresponding to $(TiC)_2^+$, $(TiC_2)_2^+$, and $(TiC_2)_4^+$. Complete characterizations of this and other nanoparticles are currently under active investigation in our laboratory.

Conclusions

We have developed a new method for the synthesis of nanoparticles of controlled size and composition. Our preliminary results appear to demonstrate the feasibility and the promise of the new method. With this method, the size of the particles can be conveniently controlled by careful control of the degree of supersaturation which is accomplished by adjusting the temperature gradient, total pressure, and partial pressure of the metal vapor generated by laser vaporization in a diffusion cloud chamber. The method can be applied to the synthesis of nanoparticles generated from virtually any metal or other involatile materials such as fullerenes (C₆₀, C₇₀, C₈₄, etc), polymers, refractive, semiconductor, and superconductor materials. The nucleating ability of these species under controlled conditions of temperature and vapor supersaturation is related to both analytical applications and to the development of new materials with unusual properties such as aerosol particles containing metallic cores and gas-phase polymerization catalyzed by metal oxide nanoparticles. We also briefly mention here several other opportunities created by the development of this simple method, several of which are planned: (i) In situ synthesis of specific catalysts (e.g., metal/metal oxide systems) of different sizes and compositions. (ii) Design of new nanomaterials such as mixed oxides/nitrides or carbides/nitrides, etc. (iii) The method can be easily scaled up to produce large quantities of the nanoparticles. (iv) The use of a cloud chamber with laser vaporization provides a new and efficient source to generate very large clusters and nanoparticles for gas-phase studies. This will require the use of small pinholes to transfer the nanoparticles into vacuum for spectroscopic, reactivity, and mass spectrometric studies. This might permit the routine extension of clusters studies to much larger systems, which are assuming an increasing importance in recent years.^{20,21}

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