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Combustion of multiphase reactants for the synthesis of nanocomposite materials

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Abstract

Controlling nanocomposite composition and morphology is a vital step toward designing new and advanced materials. The current work presents the results of an experimental investigation of the use of mixed-phase reactants for the synthesis of nanocomposite materials. Gas-phase tetramethyltin was used as a precursor for tin dioxide (SnO₂). Metal additives were introduced to the SnO₂ synthesis system using solid-phase metal acetates as the precursors. The physical and chemical properties of the metal acetate reactants, the combustion environment and the nanocomposite materials were characterized in order to clarify the reaction processes important during synthesis of nanocomposite materials from these categories of mixed-phase reactants. X-ray diffractometry was used to determine composition and the crystalline structure of reactant and product materials. Scanning and transmission electron microscopy were used to examine particle morphology of reactant and product materials, and X-ray energy dispersive spectroscopy was used for elemental speciation. The results indicate the metal acetates are an excellent source of metal and metal oxide additives in a flame reactor. The metal acetates rapidly decompose and experience considerable restructuring, leading to metal additives with a range of microstructures in the SnO₂ nanocomposites: from metal encapsulation in SnO₂ to mixed aggregates.

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1. Introduction

Many engineering applications can be improved through the use of nanocomposite materials. For example, gas-sensor sensitivity has been increased by orders of magnitude by incorporating dopants within nanocrystalline gas-sensing materials [1,2]. Core–shell nanostructures of silica and gold have been used to create particles with incredible plasmon resonance tunability, spanning from 650 nm to 6 µm [3]. Metal shells surrounding core nanomaterials have been demonstrated as having excellent potential for developing advanced bioengineering diagnostics and treatments using electro-optical interactions [4]. Room-temperature blue laser emission has been demonstrated using core–shell structures of CdS/ZnS nanocomposites [5]. Although these examples represent diverse material systems and ap-

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plications, a common feature of the nanocomposite systems is the strong dependence of the performance characteristics on the nanocomposite properties, including the relative morphology, phase, composition, size, loading, and distribution of the component species.

A novel method for the synthesis of nanocomposite materials has recently been demonstrated by Miller et al. [6]. The synthesis method uses solid- and gas-phase precursor reactants to create nanocomposite materials, and the demonstration studies showed good control of nanocomposite properties using the synthesis conditions for production of tin dioxide (SnO₂) doped with various materials [6]. Tin dioxide nanocomposites are of substantial interest as catalysts, as optical materials, and as materials in semiconductor gas sensors.

The mixed solid- and gas-phase combustion synthesis approach demonstrated at the University of Michigan has considerable potential for materials fabrication. The use of solid-phase precursor reactants combined with gas-phase precursor reactants expands the parametric range of microstructural properties that can be achieved beyond most gas-phase combustion synthesis methods. For example, staged decomposition of the reactant precursors can be used to control the relative growth rates of the condensed phase products, which dictate (in part) the morphology of the product materials. In addition, there are a large variety of nontoxic, relatively inexpensive, metal organic solid-phase materials that can be considered for design of the microstructural properties in combustion synthesis. A challenge associated with this approach is the lack of understanding of the physical and chemical mechanisms important in mixed-phase combustion synthesis systems.

Based on this need, the primary objective of the current work was to identify the combustion processes and reactant characteristics affecting the microstructural properties of nanocomposite materials fabricated using a combination of solid- and gas-phase precursor reactant materials. Links between the properties of the solid-phase reactants (such as particle size and chemical structure) and the condensed-phase products are critical for designing composition and microstructure of a nanocomposite. Improved understanding of these links will greatly facilitate expansion of the combustion synthesis method to additional material systems and applications. In order to meet the objective of the study, the synthesis environment was characterized, and analyses of the reactant and product particles were conducted to identify and quantify the properties as a function of the reactor conditions. The results are discussed in terms of potential reaction pathways.

2. Experimental

2.1. Combustion synthesis facility

All experiments were conducted using the combustion synthesis facility developed at the University of Michigan [6–10]. The facility consists of three major components: the burner (a multi-element diffusion or Hencken burner, Research Technologies, RD1X1) used to create the high-temperature synthesis environment, the bubbler system used to provide the tetramethyltin (TMT) precursor for the tin dioxide particles, and the particle feed system (PFS) used to provide the solid-phase precursor reactants.

The burner consists of an array of hypodermic fuel tubes (i.d. 0.51 mm) and oxidizer channels (i.d. 0.81 mm) arranged in a 2.54 cm square hastalloy honeycomb matrix. The matrix is surrounded by an additional 1.0 cm wide nitrogen (N₂, 28.3 lpm, Cryogenic Gases, 99.998%) shroud region. The H₂ (2.78 lpm, Cryogenic Gases, 99.99%), O₂ (1.46 lpm, Cryogenic Gases, 99.99%), and Ar (17.1 lpm, Cryogenic Gases, 99.998%) rapidly mix above the surface of the burner, creating a primary flame sheet made of diffusion flamelets. At heights >5 mm and regions >4 mm radially from the center of the burner (where the secondary fuel tube is located; see Fig. 1), the primary flame system is nearly uniform and one-dimensional in temperature, pressure, and composition. The high-temperature region, with temperatures ranging from 1400 K near the burner surface to 400 K 30 cm above the burner surface, forms the reaction environment for the particle synthesis. All flow rates are monitored using a mass flow meter (O₂: TSI, model 4100, ±2% accuracy) and calibrated rotameters (H₂, Ar, N₂: Omega, ±5% accuracy). A detailed description of the primary flame system is available [7].

For the current work, the gas- and solid-phase precursor reactants are introduced simultaneously into the synthesis environment through the secondary fuel tube located at the center of the burner (see Fig. 1). Vapor-phase TMT (Sn(CH₃)₄, Alfa Aesar, 98%) is directed to the burner by bubbling Ar (63.5 mlpm) through a reservoir of liquid TMT maintained at room temperature. Previous characterization studies indicate the high vapor pressure of the TMT (~11 kPa at room temperature) yields saturated mixtures of 21–23% TMT dilute in Ar (mole basis) [9,10]. The argon flow rate is monitored using a calibrated rotameter (Omega, ±5% accuracy).

The PFS introduces solid-phase reactants as precursors for the metal additives to the nanocrystalline SnO₂. Similar particle-feed systems have been used in combustion studies of coal particles [11,12]. The PFS system presented here is based upon those designs. A detailed schematic of the PFS, which consists
of an enclosed glass entrainment column, syringe, and syringe pump, is presented in Fig. 1. The glass column has a gas inlet diameter of 3.70 mm and an outlet diameter of 1.07 mm. Argon is used as the carrier gas through the column and is regulated by a calibrated rotameter (Omega, ±5% accuracy). Precursors are injected into the column via an open-ended, cylindrical syringe (BD 1 ml U-100), where the tip of the syringe is placed at the centerline of the column. The injection feed rate is controlled by a syringe pump (Medfusion 2001). A mechanical agitator contacts the syringe to reduce the effects of particle accumulation and to provide a steadier feed rate. During a typical experiment, the argon flow rate to the PFS is set at 390 mlpm and the syringe plunger rate is set at 1.0 ml/h (corresponding to ∼1.4 g/h for gold acetate). For all experiments, the solid phase precursor reactants were sieved to <45 µm to facilitate the particle flow through the PFS.

The flow from the PFS and the flow from the TMT bubbler mix in a glass L-shaped connector (see Fig. 1). The vapor- and solid-phase precursors are then directed through the secondary fuel tube into the reactive environment above the surface of the burner. The flow of particle precursor reactants forms a slightly lifted laminar diffusion flame. For the flow rates considered in this work, the Reynolds number based on the total argon flow rate and the i.d. of the secondary fuel tube is Re = 720. The height of the secondary flame is typically between 12 and 25 cm, based on the luminous region of the flame.

2.2. Flow-field diagnostics

Temperature profiles in the primary and secondary flame regions were determined using uncoated thermocouples (type S, Pt/10%Rh–Pt, with bead diameters of 0.050 and 0.125 mm). The measurements were corrected for radiation effects and for changes in bead diameter and emissivity due to deposition of material onto the thermocouple bead (which only affect measurements made within 4 mm of the secondary flame region). Uncertainties in the temperature measurements are estimated as ±50 K.

Particle velocities were examined for the aluminum acetate system using a high-speed digital cam-
2.3. Particle sampling, preparation and analysis

Scanning electron microscope (SEM, Philips XL30 Series) imaging of the morphology and size of the unburned metal acetate particles was achieved by depositing ~10–20 mg of the powders onto conductive copper tape. A 15-nm-thick layer of Au/Pd was then sputtered onto the samples to improve imaging quality. Samples of the as-received metal acetates and final product materials (sampled using a cold plate at height at 27 cm) were analyzed using X-ray diffraction (XRD), with a typical sample size of ~0.10–0.20 ml. The paste (0.5 ml) was spread on a glass slide and dried at room temperature for ~10 min. Scans for phase identification and for average additive particle size were obtained using an automated Scintag Theta–Theta XRD with increments of 0.02° 2θ and CuKα radiation (λ = 1.5405 Å). The scans were obtained over a 2θ range of 15°–85° at a scan rate of 5° 2θ/min. Spectral scans for average crystallite size for SnO₂ were measured over a 2θ range of 22°–31° at a scan rate of 0.5° 2θ/min. Peak positions and relative intensities of the powder patterns were identified by comparison with reference spectra [13].

The average crystallite size was determined from the XRD spectra using the Scherrer equation,

\[ d_{\text{XRD}} = \frac{0.9λ}{β_{1/2} \cos θ}, \]

where \( d_{\text{XRD}} \) is the average crystallite size, \( λ \) is the source wavelength, \( β_{1/2} \) is the full width at half-maximum of the peak used for the analysis, and \( θ \) is the XRD scattering angle of the peak.

Transmission electron microscopy images (TEM, Philips CM12 and JEOL 3011 high-resolution electron microscopes) were obtained of the final product powders and as a function of location above the surface of the burner. The samples were obtained by direct deposition onto TEM grids (3 mm diameter, Electron Microscopy Sciences, carbon film, 300 mesh copper) rapidly inserted into the secondary flame or the exhaust region. X-ray energy dispersive spectroscopy (XEDS) was used for elemental speciation.

2.4. Analysis of micrograph images

Automated image analysis of combustion-generated particles can be challenging due to highly aggregated, overlapping, and necked features. Often manual counting is employed for better feature identification. In the current work, a semiautomated method was developed to assist the manual counting and greatly decrease the time required to generate statistically significant particle size distributions. The method automates the accounting of feature sizes, leaving feature identification to be performed manually.

The first step of the process is to duplicate the particle features in a vector graphics package (e.g., CorelDraw or Adobe Illustrator). The features of interest (e.g., primary spherical particles) are identified in the image by overlaying equivalent outlines on the features. The overlays are then aligned in a column with no overlap between features and extracted to a binary (black and white) bitmap file—with either a 1 or 0 value for each pixel. Such a file can be analyzed using automated software (e.g., Matlab) to extract the particle size distribution by counting the zeros in the central column of each feature and applying the appropriate scale. In the current work, the particle size distributions were extracted assuming spherical particles; however, the technique can be easily adapted to more complex shapes. As a demonstration of the method, Fig. 2 presents an image of overlapping spherical gold particles. Image analysis resulted in an average particle diameter of 0.86 ± 0.35 µm, which is within the manufacturer specifications (Alfa Aesar, 99.96% Au) of 0.5–0.8 µm.

3. Results

3.1. Characterization of unburned solid-phase reactants

Table 1 provides a summary of the solid-phase precursors investigated and their thermophysical properties. The most critical data for this study are the decomposition temperature and the density of the solid-phase reactants. Estimates were available for all the metal acetates considered, except the gold acetate. As a consequence, efforts were made to determine these properties using simplified yet quantitative methods. The as-received gold acetate was analyzed using a
displaced gas volume method (Micromeritics, AccuPyc 1330) to determine the particle mass density listed in Table 1. The decomposition temperature of the gold acetate was estimated using a visual melting temperature tool (MEL-TEMP 3.0). A sample of the unreacted gold acetate (∼20 mg) was placed in a capillary tube (i.d. 0.9 mm). The tube was heated (5 °C/min) and the sample observed. The decomposition temperature was approximated as the temperature at which a dramatic change in the color of the powder took place, from light brown to a dark brown. The decomposition temperature determined for gold acetate was 150–160 °C, which is consistent with other metal acetate data (see Table 1). Additionally, this method reproduced a palladium acetate decomposition temperature of 222–229 °C, which is in good agreement with the literature value of ∼240 °C [14].

Fig. 3 presents SEM images of as-received metal acetate powders. As seen in the images, gold and aluminum acetates appear as porous and irregular structures, while copper and palladium acetates appear as condensed and well-defined crystalline structures.

Typical XRD patterns of the as-received unreacted gold, aluminum, copper, and palladium acetate powders and corresponding reference patterns are presented in Fig. 4. There are no standards available for gold acetate in the JCPDS database [13]. However, Kritl and Drofenik [15] presented an XRD scan of gold acetate in their article on sonochemical preparation of Au3S3, which is reproduced in Fig. 4a for reference. The spectra agree well with respect to location of the peak features and relative intensities. Note the copper acetate spectra (see Fig. 4c) indicated the presence of both copper acetate (24-1126) and copper acetate hydrate (27-145) in the precursor powder.

Table 2 provides a summary of the average crystallite sizes determined from the metal acetate XRD spectra ($d_{XRD}$). Note that an average crystallite size for palladium acetate could not be accurately determined due to interference from multiple peak features. The crystallite sizes obtained from the metal acetate XRD spectra suggest that the particles presented in Fig. 3 consist of crystallites approximately 12 nm in size for the aluminum acetate, 26 nm in size for the copper acetate, and 160 nm in size for the gold acetate.

### 3.2. The combustion synthesis environment

Temperature profiles for the combustion synthesis system with and without the presence of the secondary flame are presented in Fig. 5 as a function of height above the surface of the burner. No solid-phase precursors were used in these characterization studies. The thermocouple was located slightly off-center of the burner (see inset in Fig. 5) for both data sets. The presence of the TMT flame leads to higher temperatures throughout the synthesis region encountered by the particles. Particle residence times based on the particle tracking are presented in the inserts.

### 3.3. Characterization of particle evolution

The evolution of particle microstructure throughout the combustion synthesis environment was examined for the gold acetate/TMT system using particle sampling and ex situ imaging at increasing sampling heights. The series of TEM images presented in Fig. 5 (bottom panel) show the progressive formation and growth of the Au/SnO2 nanocomposites. Gold particles are formed early in the system (5 ms) with relatively few discrete, small SnO2 particles present. As the residence time increases, the frequency of appearance of the gold particles increases slightly; however,
### Table 1

Thermophysical properties of bulk condensed-phase materials relevant to the material synthesis systems studied

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Name</th>
<th>Molecular weight (CAS #)</th>
<th>Reactant manufacturer, purity</th>
<th>Melting point (K)a</th>
<th>Boiling point (K)</th>
<th>Vapor pressureb (atm)</th>
<th>Density (g/cm³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)(C₂H₃O₂)₂</td>
<td>Aluminum diacetate</td>
<td>162.163 [142-03-0]</td>
<td>Sigma–Aldrich, N/A</td>
<td>327</td>
<td>N/A</td>
<td>–</td>
<td>1.74</td>
<td>[13,19]</td>
</tr>
<tr>
<td>Cu(C₂H₃O₂)₂·H₂O</td>
<td>Copper(II) acetate monohydrate</td>
<td>199.650 [6046-93-1]</td>
<td>Alfa Aesar, 99.99% at 513 K</td>
<td>388</td>
<td>Decomposes at 513 K</td>
<td>–</td>
<td>1.88</td>
<td>[19]</td>
</tr>
<tr>
<td>Pd(C₂H₃O₂)₂</td>
<td>Palladium acetate</td>
<td>224.507 [3375-31-3]</td>
<td>Sigma–Aldrich, 98%</td>
<td>478</td>
<td>Decomposes at 480–570 K</td>
<td>–</td>
<td>3.00e</td>
<td>[14]</td>
</tr>
</tbody>
</table>

#### Intermediate and product species

| Cu    | Copper   | 63.546 [7440-50-8] | 1358 | 2868 | 4.38 × 10⁻³ | 8.96 | [19] |
| Cu₂O | Cuprous oxide | 143.091 [1317-39-1] | 1508 | Decomposes at 2073 K | – | 6.00 | [19] |
| CuO   | Cupric oxide, copper oxide | 79.545 [1317-38-0] | 1719 | N/A | – | 6.31 | [19] |
| PdO   | Palladium(II) oxide | 122.42 [1314-08-5] | Decomposes at 1023 K | – | 8.3 | [19] |
| Sn    | Tin      | 118.71 [7440-31-5] | 504 | 2875 | 3.94 × 10⁻³ | 7.27 | [19] |
| SnO₂  | Tin dioxide, tin(IV) oxide | 150.709 [18282-10-5] | 1903 | N/A | – | 6.85 | [19] |

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a Metal acetate melting points are too close to the decomposition temperature to differentiate.
b At 2000 K.
c Estimated using a visual melting tool (MEL-TEMP 3.0).
d As determined using a density analyzer (Micromeritics, AccuPyc 1330).
e Estimated density [14].

The gold particles are always spherical and sparsely located. The tin oxide is initially present in infrequent, small clusters; the primary particles develop as the height increases; and a larger degree of agglomeration begins approximately 3.5 cm above the burner.

The results of the semiautomated image analysis of the particle size distribution of the SnO₂ particles and typical SnO₂ particle morphologies are presented in the top panel images of Fig. 5. The average SnO₂ particle size and the lognormal distribution are provided for each residence time and sampling height. As the residence time increases, the average particle size grows from ~7 to 13 nm and the lognormal distribution becomes more representative of the population, as indicated by an increased quality of fit to the experimental data.

### 3.4. Characterization of final nanocomposite materials

The effects of the operating conditions and solid-phase reactants on the final product morphology, average SnO₂ crystallite size, and metal loading are reported in detail in Miller et al. [6]. The results of that study are briefly summarized here for reference. The average SnO₂ crystallite size of the product pow-
ders could be varied compared to a baseline undoped SnO₂ synthesis condition using the additives and the burner operating conditions. Metal or metal oxide additives were created (as determined via XRD spectra) depending on the precursor used. For example, only metallic gold was identified from the XRD spectra of the nanocomposite materials made using gold acetate and TMT, whereas copper oxides were formed when copper acetate and TMT were used. A range of microstructures was observed from partial encapsulation of the metal additive within a layer of SnO₂ particles to mixed material systems. The metal acetates typically produced metal additive particles that were readily identifiable by the size, crystalline structure, and contrast in the TEM images (see [6] for examples).

XRD spectra of the Au/SnO₂ nanocomposites produced using gold acetate and tetramethyltin are presented in Fig. 6. Typical morphology of these nanocomposites is presented as the inset in Fig. 6. The XRD data demonstrate that the SnO₂ is in the cassiterite phase and the gold is present in metallic form. XRD analyses of the average crystallite size for the SnO₂ particles and how the SnO₂ is affected by the presence of the metal additives are presented in detail in Miller et al. [6]. XRD analyses of the metallic gold peaks conducted as part of the current work yielded an average particle size of 80 nm for the gold in the nanocomposites, which is in excellent agreement with the TEM imaging results conducted previously, where an average value of 83 nm was determined [2].

The aluminum acetate system was unusual compared to the other metal acetates, in that no metals or metal oxides (besides SnO₂) were identified in the XRD spectra. Additionally, it was challenging to detect aluminum additives in the TEM images using contrast or crystalline structure. After considerable analysis, some particles were identified as containing aluminum using XEDS. Such an example is presented in Fig. 7. The particles are noticeably smaller than the SnO₂ particles and appear highly fused.

Although the TEM data indicate the presence of discrete metal additive particles, trace quantities of the metal additives may also be present within the SnO₂ particles, but below the detectable limits of TEM XEDS. The relatively high vapor pressures of the metals associated with the metal acetates support this possibility. Table 1 presents the melting and boiling points of the pure metal species associated with the metal acetates. The metal vapors in the reactor can reach high concentrations with mole fractions on the
Fig. 4. XRD spectra of as-received unreacted (a) gold acetate, (b) aluminum acetate, (c) copper acetate, and (d) palladium acetate.

Table 2
Comparison of average crystallite size based on XRD analyses of as-received metal acetates, predicted metal additive size based on Eq. (2), and TEM-observed metal additive particle dimensions

<table>
<thead>
<tr>
<th>Precursor</th>
<th>2θ feature used with Eq. (1) (°)</th>
<th>d&lt;sub&gt;XR&lt;/sub&gt;D (nm)</th>
<th>Metal additive product</th>
<th>d&lt;sub&gt;Me&lt;/sub&gt; (nm)</th>
<th>d&lt;sub&gt;p,TEM&lt;/sub&gt; (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold acetate</td>
<td>15.4</td>
<td>160</td>
<td>Gold, Au</td>
<td>63.4</td>
<td>83</td>
</tr>
<tr>
<td>Au(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum acetate</td>
<td>19.6</td>
<td>12</td>
<td>Aluminum oxide</td>
<td>9.8</td>
<td>12</td>
</tr>
<tr>
<td>Al(OH)(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>11.4 (Cu(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>26&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Copper oxide</td>
<td>12.8 (CuO)</td>
<td>50</td>
</tr>
<tr>
<td>Copper acetate</td>
<td>12.9 (Cu(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;·H&lt;sub&gt;2&lt;/sub&gt;O)</td>
<td></td>
<td></td>
<td>19.9 (Cu&lt;sub&gt;2&lt;/sub&gt;O)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Average based on the anhydrate and hydrated copper acetate.

order of hundreds to thousands of parts per million. These gas-phase species are highly mobile and likely to condense on existing nanoparticles as the temperatures in the reactor decrease.

4. Discussion

Solid-phase precursors can react in a variety of manners in a high-temperature environment. For example, the particles can decompose or explode, yielding reactive intermediates in the gas, solid, or liquid phases; or the particles can burn in a fashion similar to coal particles where volatiles are emitted, followed by reaction with the remaining particle “char.” For metals, the burning process can entail gas-phase oxidation of evaporated metal, surface oxidation leading to a volatile or suboxide species, or surface oxidation leading to a nonvolatile oxide deposit, which may dissolve into the molten metal [16]. Combustion
of pure metals has also been observed to be explosive, resulting in particle fragmentation and dispersion [17].

The experimental data obtained in the current work indicate the solid-phase metal acetates rapidly decompose at the temperatures found in the combustion synthesis environment. Specifically, the presence of spherical gold particles at low sampling heights/short residence times (see Fig. 5) indicates the conversion from solid-phase metal acetate to gold nanoparticles occurs in less than 5 ms. In addition, no gold aggregates or agglomerates were observed at any sampling location, demonstrating the sintering process between gold particles must occur virtually instantaneously. Indeed, calculations for the characteristic time for gold nanoparticle sintering [18] yielded values below 100 µs for regions near the surface of the burner.

The Au particles produced in the nanocomposite system can be compared with the gold acetate precursor as a means to determine if there is a relationship between the parent and child materials. Such a connection, if it exists, would be valuable for predicting nanocomposite morphology. Assuming spherical particles, the size of the gold particle (the child particle) is related to the gold acetate (the parent particle) via

\[ d_{Me} = \left( N \frac{\rho_{MeAc}}{\rho_{Me}} \frac{MW_{Me}}{MW_{MeAc}} \right)^{1/3} d_{MeAc}, \quad (2) \]

where \( N \) is the molar conversion factor, \( \rho \) is the density and MW is the molecular weight. The subscripts Me correspond to metal and MeAc correspond to metal acetate. Using the densities and molecular weights listed in Table 1 for gold and gold acetate and assuming a one-to-one molar conversion rate, Eq. (2) yields \( d_{Au} = 0.45d_{AuAc} \). Recall that an average gold particle size of \( d_{Au} = 83 \text{ nm} \) was determined based on the Au size distribution measured from the TEM images [2]. When Eq. (2) is used to estimate the characteristic dimension required for gold acetate to directly form 83-nm-diameter particles, a value of \( d_{AuAc} = 186 \text{ nm} \) is determined. This value is very close to the average crystallite size of 160 nm determined using XRD of the gold acetate.
Fig. 6. XRD spectra of Au-doped SnO$_2$ powder produced using gold acetate as the additive precursor. The features and lattice parameters associated with the cassiterite phase of SnO$_2$ (21-1250) [13] and metallic gold (4-784) [13] are indicated in the figure. The inset presents a typical TEM image of the nanocomposites. The larger high-contrast particle was identified as Au using TEM-XEDS.

Using the average crystallite size from the XRD analysis of the solid-phase reactants and the appropriate data from Table 1, Eq. (2) can be applied to determine the size of metal particles in nanocomposite materials produced using the aluminum acetate and copper acetate precursors. Table 2 provides the metal particle dimensions for the aluminum and copper systems for the appropriate molar conversions from the precursor crystallite sizes ($d_{XRD}$). TEM images of aluminum and copper acetate products indicate typical particle sizes ($d_{p,TEM}$) of approximately 12 and 50 nm for alumina and copper oxide, respectively. Note, the TEM values are biased to larger sizes (smaller particles are more convolved with SnO$_2$ particles and therefore more difficult to identify), and because the additives are sparsely located in the TEM images, the size estimates have high uncertainties. There is good correlation between the metal particle sizes ($d_{Me}$) and the measured dimensions ($d_{p,TEM}$) for the gold and aluminum acetates, while there is over a factor of 2 difference for the copper acetate. The discrepancy may be due to different physical decomposition mechanisms for the metal acetates. Specifically, the porous precursor materials may undergo additional particle fragmentation which may not occur for the solid-phase reactants with limited porosity.

The SEM images of the metal acetates show remarkable differences in the structures of the materials. Combined with the data of Table 2, the results indicate that morphological differences in the precursor materials may affect the final metal additive dimensions, particularly for gold and aluminum acetate which exhibit appreciable porosity. The porous structure supports the theory that the acetate particles can fragment, potentially along grain boundaries, due
to increased pressure within the pores as the metal acetate vaporizes and decomposes. The metal atoms nucleate locally, and these nanoparticles undergo collision to form aggregates and agglomerates. If the sintering rates are high, as is the case for gold nanoparticles, spherical particles are formed with dimensions on the order of the grain size of the gold acetate. Fig. 8 presents a schematic representing the steps of metal acetate decomposition and metal particle formation suggested by the results for the porous materials. When the copper and palladium acetates vaporize and decompose, these denser structures may not fragment along grain dimensions. Without the additional fragmentation, neighboring grains can coalesce to form larger particles as observed in the TEM images [6].

A schematic integrating the gold acetate and TMT systems during the formation of nanocomposites is
presented in Fig. 9, where the early gold acetate decomposition processes are omitted for clarity. The presence of the metal additives can affect the SnO\(_2\) formation and growth processes in a variety of complex ways. The metals can induce new reaction pathways via homogeneous and heterogeneous catalysis. The temperature and flow fields can be altered when the additive precursors are introduced. The metal additives can modify the SnO\(_2\) grain growth kinetics and provide sites for heterogeneous deposition and SnO\(_2\) particle growth. Based on the results of the current study, the spherical gold nanoparticles are presumed to interact with SnO\(_2\) primarily through interparticle collision and aggregation and as sites for surface growth. The coalescence of SnO\(_2\) is slower than that of gold, resulting in the agglomerated structures.

5. Conclusions

Controlling nanocomposite morphology is a vital step toward designing new and advanced optical, semiconductor, catalyst, and sensor materials. In particular, encapsulation of metals has yielded remarkable photonic properties. Combustion synthesis methods offer the potential to produce such high-value-per-gram materials at high rates with good control of the nanocomposite properties. The results of the current work indicate that metal acetates provide an excellent source for metal additives in flame synthesis environments. Metal acetates can also provide access to nanosized additives, where the approximate dimension of the metal additive can be predicted using the grain size of the parent material. The formation of nanodimensioned metals and the ease of handling, low toxicity, and relatively low cost of metal acetates point toward a promising new scope for the synthesis of nanocomposite materials.

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