Microscale thermogravimetric device analyzes nanoparticle purity and coatings

Elisabeth Mansfield and Timothy P. Quinn

A new chemical-analysis technique uses the shifting, ultrasonic pitch of a small quartz crystal to determine the composition of samples of only a few micrograms of material.

Nanoparticles have piqued the imaginations of scientists and engineers because of the unique properties that stem from their size and surface-area-to-volume ratio. For example, it has been proposed that carbon nanotubes (CNTs) may be used as the next generation of interconnects in electronics manufacturing. It has also been proposed that gold nanoparticles could be used to make insoluble cancer drugs soluble and active only against specific tumor cells. With the burgeoning number of applications, there is an increasing need for techniques that can accurately measure the purity and other properties of nanoparticles.

Scaling down conventional instrumentation to match the need for nanoscale characterization has been difficult. In some cases, the tools used on the bulk scale are unable to provide the same quality of information. For example, thermogravimetric analysis (TGA) measures the reaction energy needed to decompose, oxidize, dehydrate, or otherwise chemically change a sample with heat. Conventional TGA measurements require samples of several milligrams or more of material, which makes it difficult to measure nanoscale materials: several milligrams may represent the entire production run or the amount recovered after exposure to the environment. Other methods, such as transmission-electron microscopy, can be used to characterize nanoparticles with reasonable sample sizes, but these techniques are expensive because of the extensive analysis period required to gather statistically relevant data.

If we are to scale the ideas used to make conventional TGA measurements to the micro- or nanogram scale, the measuring device needs to be sensitive to nano- or picograms. A possible choice for achieving this level of precision is the quartz-crystal microbalance (QCM). QCMs are highly sensitive acoustic devices capable of monitoring subpicogram mass changes in rigid coatings and thin films. These devices are typically composed of a thin, piezoelectric, temperature-compensated (so-called ‘AT-cut’) quartz crystal sandwiched between two metal electrodes. Any perturbation of the crystal surface (e.g., adsorbed mass) alters the crystal’s characteristic resonance frequency in a predictable way, allowing one to readily determine mass changes at the near-molecular level.

We have used QCMs at elevated temperatures to characterize decomposition kinetics in a manner similar to that of TGA. To demonstrate this method, we analyzed representative materials by the heated-QCM technique and then compared the results to analogous TGA measurements. Selected materials included those that exhibited mass loss at high temperatures, some that showed mass loss at low temperatures, and mixtures of these materials in which multiple reactions occur. Complex materials, such as CNT samples (see Figure 1), which can comprise different geometries within a single sample, were also analyzed.

Figure 1. Carbon-nanotube thermogravimetric analysis (TGA) as measured by conventional methods (blue line) and quartz-crystal microbalance (QCM)-TGA (red points). Reprinted with permission.
to provide an example of heterogeneous sample analysis. This method showed strong correlation between heated-QCM and conventional TGA measurements, where the heated-QCM measurements follow the conventional decomposition profile.

We also extended the use of this heated-QCM method to characterize other types of nanomaterials. We evaluated CNT samples from different manufacturers for metal-catalyst content and oxidation temperature, which provide a measure of their thermal stability. Differences between manufacturers can easily be seen by microscale TGA measurements, from samples 1000x smaller than conventional TGA measurements. This method will become increasingly valuable as CNTs of one type (i.e., single-chirality) can be achieved.

Determining the coating density on gold nanoparticles has also been a difficult task for nanomaterial characterization. We have applied microscale TGA to quantitatively measure coverage of gold-nanoparticle surfaces with poly(ethylene glycol) coatings. We compared our measurements by microscale TGA to conventional methods—such as nuclear magnetic resonance and fluorescence spectroscopy—to evaluate coating density and found comparable results.

External heating of the QCM has allowed for measurements of a variety of materials in a multiplexed manner, but to better match the TGA measurements, continuous monitoring of the sample as it is heated has to be accomplished. We have developed a QCM with an onboard resistive heater to allow for simultaneous heating of the sample and monitoring of weight (see Figure 2). This in situ-heated QCM has been successfully used up to 250°C to monitor the decomposition of low-temperature materials and will be used to monitor nanoparticle coatings, purity, and composition in the future.

In summary, to provide sufficient characterization of nanomaterials, instrumentation needs to be scaled to a level appropriate to today’s microgram-sized samples of nanoparticles. Through application of QCMs at high temperature, the National Institute of Standards and Technology has paved the way for realization of microscale TGA measurements for nanoparticle samples. Work continues to provide higher-temperature operation, increased sensitivity, and user-friendly designs for nanoparticle-monitoring systems.

Author Information

Elisabeth Mansfield and Timothy P. Quinn
National Institute of Standards and Technology (NIST)
Boulder, CO

Elisabeth Mansfield has a PhD in analytical chemistry from the University of Arizona. She joined NIST in 2007 as a postdoctoral fellow and is now a research chemist in the Materials Reliability Division.

References
8. Provisional US patent, provisional serial number 61/304,815, NIST.