Resonating Platforms for Nanomaterial Analysis

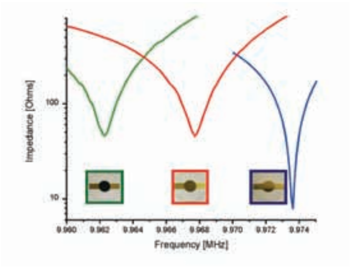
Objective

Our goal is to develop novel resonating platforms with enhanced mass sensitivity, based on quartz crystal microbalances (QCMs) and MEMS oscillators. These high-resolution mass sensors are needed to quantify fate and transport issues for nanoparticles in biological environments and in water systems, as well as for advanced characterization of nanoparticle chemistry. By reducing the required sample volume and increasing sensitivity, dynamic changes in surface chemistry and interface stability can be monitored in gas or liquid environments in real time.

Impact and Customers

- Characterization of nanoparticle chemistry remains a key challenge for material suppliers. Methods to rapidly detect small variations in material composition are needed for quality control during manufacture.
- Numerous nanoparticle compositions are now produced commercially in large volumes with little data available on toxicological response. Methods to rapidly quantify fate and transport issues (e.g., nanoparticle uptake by specific cells) as a function of surface chemistry, surface charge, particle size, and particle shape are needed to screen nanomaterials for potential safety issues.
- Nanoparticles are also being developed for water remediation. In these applications, changes in surface chemistry and charge due to interaction with the water system can greatly reduce nanoparticle effectiveness. New characterization tools are needed to monitor reactions at the nanoparticle-water interface.
- The development of innovative resonant NEMS devices with high quality factors (*Q*s) in liquid offers the potential of achieving orders-of-magnitude increases in sensitivity of molecular detection/characterization in healthcare diagnostics and water-quality testing, while simultaneously reducing costs relative to conventional macroscopic measurement platforms.

Approach

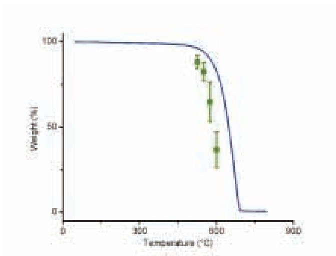


Quartz crystal microbalances (QCM) are highly sensitive acoustic devices capable of monitoring sub-picogram mass changes in rigid coatings and thin films. Devices are typically comprised of a thin piezoelectric AT-cut quartz crystal sandwiched between two metal excitation electrodes. When an AC voltage is applied to the electrodes, the quartz crystal oscillates at a characteristic frequency based on the crystal geometry, referred to as the resonant frequency. Any perturbation of the crystal surface (*e.g.*, adsorbed mass) alters this characteristic frequency. To determine mass changes in the material coating, we monitor the resonance frequency of the quartz crystal using an impedance analyzer. During coating deposition, the resonance frequency decreases, with the shift in frequency directly proportional to the change in mass. On heating, the coating mass decreases due to oxidation of the carbon material, resulting in an increase in resonance frequency.

Because of their sensitivity and stability, QCMs are used to monitor film thickness during deposition; detect toxic and hazardous gas species; and assess moisture, humidity and dew point levels. These devices are also being explored for emerging applications in the areas of life sciences, polymer processing, and nanotechnology. We have developed an elevated temperature quartz crystal microbalance technique that interrogates samples on the order of 1 microgram or less. This elevated temperature platform allows for thermogravimetric measurements to be made on samples 3 orders of magnitude smaller than commercially available thermogravimetric analysis (TGA), resulting in cheaper, rapid collection of statistically significant populations of data for monitoring nanoparticle purity. QCM measurements on nanoparticles in aqueous environments are being used to determine the feasibility of nanoparticle use in water remediation.

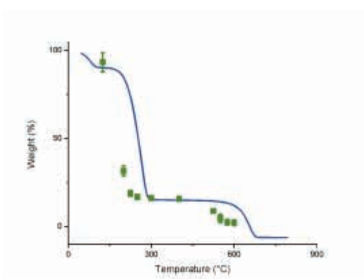
Accomplishments

We validated our elevated temperature QCM method using materials with simple thermal profiles. We first characterized the bulk materials by TGA, identifying their oxidation temperature. Using this temperature as a guide, we then treated multiple crystals over a temperature range around this oxidation temperature and compared mass loss and homogeneity data with the results from TGA.



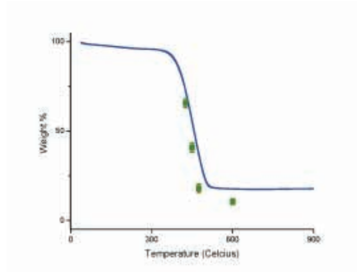
TGA (blue) and QCM (green) measurements of carbon black material.

Once the QCM measurements were shown to closely follow the TGA curve for materials with simple thermal decompositions, we extended the technique to include mixtures of these materials to demonstrate the capabilities of monitoring more complex samples.



Comparison of TGA and QCM data for a mixture of Pluracol and carbon black.

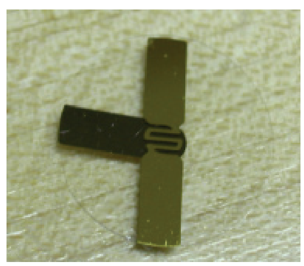
We also evaluated several commercial-grade carbon nanotube materials with different degrees of chemical purity.



TGA and QCM measurements of a representative carbon nanotube sample.

For a relatively pure nanotube specimen, we were able to closely approximate the TGA data, both in terms of mass loss at temperature and homogeneity. Based on results to date, the elevated temperature QCM technique can be used to evaluate carbon nanotube quality by manufacturers to test current batch-to-batch production differences.

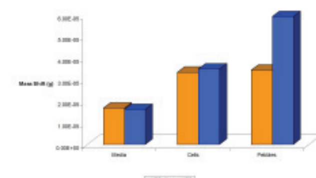
Currently, this elevated temperature QCM technique is limited by the heating process. Each heating step consists of a ramp to the desired temperature and a cooling step back to room temperature in order to measure the resonance frequency. To allow this technique to follow the decomposition of the TGA profile, continuous heating of the sample is achieved by integrating a heater onto the crystal face. With integrated heaters, the sample can be heated *in situ* while monitoring the resonance frequency. The first generation of these heaters can reach temperatures in excess of 250°C. Further development of the QCM heaters will allow for real time TGA-like monitoring of carbon nanotube samples (up to 550°C) using microgram quantities.



QCM with on-board heater.

Applications of the QCM techniques have been expanded beyond carbon nanotube samples to include analysis of interactions in water systems. Metallic nanomaterials (e.g., silver nanoparticles and zero-valent iron) are currently being investigated for water remediation. Silver nanoparticles used in ceramic membranes are monitored on the QCM to determine the leaching rate of the nanoparticles from the ceramic surface. Water conditions (e.g., pH, ionic strength) are investigated to understand the impact on nanoparticle leaching from membrane surfaces. Metallic coatings on the zero-valent iron particles increase degradation of water pollutants such as halogenated disinfection by-products.

In addition, nanoparticle uptake by cells is currently being investigated by QCM. Uptake of nanoparticles has been shown to be dependent on the surface properties of nanoparticles.



Most other uptake measurements rely on microscopic techniques to elucidate if nanoparticles have been taken up by the cell. The use of QCM for this application is unique, in that it allows the uptake to be monitored independent of the optical properties of the nanomaterials.

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Publications

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