NANORELEASE STEERING COMMITTEE WORKSHOP
MAY 10-11, 2011
CONSOLIDATED NOTES

MAIN THEMES

(1) Defining the NanoRelease project's conceptual model/framework and defining the desired outcomes may help the Steering Committee select an engineered nanomaterial / carrier system for further investigation.

(2) The Steering Committee may be able to limit the project's scope by defining likely receptor populations.

(3) It maybe helpful for the SC to consider only one phase in the life cycle when designing the release scenario.

(4) There is a need for reference materials to allow comparison to NM before addition to matrix to NM after release. They may not be the same.

(5) The SC has been using "round robin" and "inter-laboratory testing" inter-changeably, but other's do not.

- May involve testing the same sample or various labs obtaining portions from the same sample
- Wide participation is needed
- Methods must be similar for adequate comparisons
- Involves security, chain of custody and statistics.
  Maintaining information can be daunting
- Data reporting, ranges and categories
  Must consider CBI issues upfront
  Non-disclosure agreements may be helpful

Information Security

- In order to encourage broad participation and offering of information it could happen that other information needs to be protected. Transparency within the project is essential but if information does not need to be revealed for the project to accomplish its goals and the protected information doesn't detract from this then not revealing the info isn't a problem.
- The project needs to be aware of this consideration and be prepared to take needed actions.
- Examples include blending of samples so that a single source can't be identified, blinding of samples to protect the supplier identity, 3'rd party collection of information for consolidation where none of the info providers see info from others, and the like.
- The Silver Nano Working Group has been through a CBI process and may be able to share their experience.

- EPA has a lot of experience in protecting CBI and has both developed internal practices and used publicly available technology on the Internet to do so.

Specific nano-Silver Considerations

- Laundering/washing represents the most aggressive conditions textiles face, resulting in the greatest release and thus is an important release scenario
  - *Detergent impacts release*
  - *Must consider mouthing*
  - *Conditions/environment of release critical (pH, hardness, purity, etc.)*
- Particles may be >450 nm but also include pieces of the fiber; needs further characterization (Reference – Bernd Nowack)
- Nano-silver may undergo complex transformations making analysis challenging
  - *Release matrix (solution) will impact transformations*
  - *Time is an important factor in transformations*
  - *Are equilibrium processes also an issue?*
- Important to consider both the Ag+ source (e.g. n-Ag, n-AgCl, AgS) and carrier system (textile) incorporation process (i.e. master batch, finishing or surface deposition) as each of these affects release.
- Release to water is connected to known hazard data
- n-Ag is being used in many applications with anti-microbial uses among the most significant.
- Ag+ is the active species. There's little evidence of activity from n-Ag particles.

Specific MWCNT Considerations

- With sanding and other abrasive techniques, it is important to get handle on possible artifacts, but these also haven't been shown to release free CNTs.
- Weathering is the only process that results in the release of naked fibers – otherwise, nanotubes are bound in the composite resin
- Sanding, drilling, grinding may benefit from additional, more controlled, investigation for release
- Test method should include TEM and mass spectroscopy
- Compared to n-Ag, more information appears to already exist about CNT life cycles. The story is very complicated.
- Some info on SWCNT or DWCNT may apply to MWCNT but there are important differences such as trace ingredients.
  - *Don't know if these affect release but they do affect toxicity.*
- Addition of MWCNT to a polymer changed Tg.
  - *If this is a general effect it will make comparative evaluations more challenging.*

General Testing Considerations

- Size, morphology, surface coating, agglomeration state, number and number concentrations
- Protocols needed for exposure and sampling
- Instrumentation adequate but validated methods for nanomaterials is lacking
- Comparability of instruments unknown

Need standard protocols

- Link between toxicity metrics and exposure metrics not well understood
- Randomizing and aggregating data, as well as use of blind samples and randomizing methods, are important approaches for addressing confidential information
- A panelist (Cook) expressed that the minimum level of instrumentation required for NM determinations in release methods that may be one of the outcomes of the projects are TEM and Mass Spec. This panelist also recommended that the nanomaterial chosen be n-Ag. He believed that the key properties will be easier to measure.
- Another panelist (Kingston) suggested that initially high-tech tools may be needed by the Project but it may be possible to correlate results to results using "lower tech" instrumentation. He also noted that the analysis of n-Ag is complicated after release. CNT's are complicated at all times but may be more consistent before and after release.
- Another panelist (Stefaniak) voted for n-Ag
- The fourth panelist (Nguyen) noted that UV-Vis can be a good tool for CNT release and some functionalized CNT's can be analyzed by ICP-MS.
- All of the panelists and many of the Workshop participants come from places where access to high-tech toys is possible.

  The SC should not overlook that some stakeholders (e.g the NGO community) do not, so as we discuss methods we should keep their interests in mind.
- Steering Committee should try to collect info about future uses of the selected NM and not just rely on existing uses to build release scenarios. We could overlook important future uses.

BREAKOUT SESSIONS:

<u>Session 1: Risk Assessment Relevant Release Scenarios</u>

Silver

Occupational:

General agreement among both groups that abrasive processes when directly handling fabrics treated with nanosilver is of concern. This may be during material development, product development retail or end of life. Retail exposures in a warehouse scenario – handling tons of clothes routinely. Also, issue of laundry worker exposure during handling of wet treated fabrics. High energy processes such as woven materials using automated equipment could result in airborne exposures.

Consumer:

<u>Group 1</u> raised two scenarios: direct contact with socks and/or underwear containing nAg released either by sweat or chafing; and sensitive subpopulation exposure via release by chewing/saliva on a baby blanket containing nanosilver.

Group 2 also raised these scenarios and two more: release to house dust via dryer lint and clothing wear; and release to skin via wet bathing suits treated with nanosilver.

Environmental:

General agreement among both groups that clothes washing is a primary pathway of release to the environment. Also, during manufacturing, recycling of waste fiber; and end of life incineration exposure. Landfill exposure was discussed, but it was agreed this was lower levels of exposure, and slower, over time. Some discussion of fate pathways related to washing exposure – e.g. what is released and is there nanoparticle or free silver exposure.

Matrices:

Group 1 Occupational: may want to test different fabrics; nylon containing nanostructured coatings (not particles) was suggested, but not generally agreed upon. There is an issue of coating versus incorporation of nanosilver into yarn. Polyester is a common application for nanosilver that will break down with wear, however cotton coated with a binder material that contains nanoscale silver chloride may also be of interest.

Group 2 suggested looking at production volumes to select more relevant fabric type.

Materials:

Below 20 or 30 nm particles that are stable and commercially relevant, but issue of shape was raised. Could have higher availability from asymmetrical particles. On measuring what is released, this includes the intentional release of silver ions, and the unintentional release of nanosilver particles from the matrix.

MWCNTs:

Occupational:

General agreement among those who have tested these processes (e.g. Bello and David, Nguyen) that abrasive processes including cutting and drilling are high priority. Secondary processes include grinding and sanding. Liquid processes that include handling are also of concern, e.g. wind blade extrusion. Processing, including stamping, was also raised.

Consumer:

MWCNT in rubber, e.g. tires was raised, but one participant suggested this is not currently an application, or if it is, it is not widespread due to cost. Water filtration units also suggested. Releases during "recycling" of electronics during burning off to recover metals - generally outside the U.S. also boat hulls raised as a potential release scenario – owners sanding their boats.

Group 2 suggested the use of MWCNT as flame retardants in plastic as a consumer pathway, as the plastics (e.g. from computers) degrade and are released into house dust, similar to brominated flame retardants. Also, catastrophic events such as fires. Concern that at 1% loading, low exposure potential under any scenario.

Environmental:

Incineration that would remove matrix, with uncertain fate for the MWCNT. Recycling a potential scenario with chemical digestion to remove matrix. Cement

also raised but not known to be a current application. Incineration, weathering and fires are release scenarios.

Matrices:

Priority assigned to mixture of material with a matrix over nanostructured layers applied to polymers. Epoxy may be a valid matrix, but may not currently represent a lot of use. Nylon may be an alternative.

Group 2 thought epoxy was the biggest use, but that it generally comes pre-preg, or embedded. Cement, but not a current matrix.

Materials:

Discussion of modification/ functionalization.

Group 1 expressed concern over the need to validate that functionalized tubes do not modify the behavior.

Group 2 felt functionalized tubes were more representative of actual uses, and will facilitate detection.

Session 2: Release Methods

Scope - What quantitative inputs are required to develop post-release models for nanomaterial transformations, transport, and fate, and what is the state of measurement methods for these inputs?

Silver

Participants agreed that a two-step approach for assessing release (flux) was appropriate:

1. Is there a release of silver into a medium? Measured as total silver regardless of physical or chemical form
2. If so, perform follow-on studies to evaluate the forms of the released silver (ionic species, particles)

A proposed basic measure of release is: [amount of silver released (mass or number of particles)]/[total mass of silver in the product or total mass of the product]/time. This measure is valid for total silver or the individual forms of silver. Dissolution is the most likely release mechanism.

Participants also agreed that information on the silver in the matrix was not needed for this two-step approach to measure release (flux), but having such information could be useful.

Participants agreed that measurement methods were available for measurement of total silver released and would soon be available to quantify the individual released form(s) of silver:

1. Total silver – ICP-MS
2. Ionic species and particles – requires a pre-fractionation step to separate particulate from dissolved (*e.g.*, using ultrafiltration, centrifugation, field flow fractionation, ion chromatography), then analysis of mass using ICP-MS.

Participants also noted that analytical sensitivities may not be sufficient for measuring silver in a media and that pre-concentration might be needed. Caution is needed when pre-concentrating to avoid changing material characteristics.

Another area of discussion was the issue of the source of the nanoparticles. The point was raised that silver nanoparticles could form in a media via precipitation of ions released from micron scale silver particles. As such, understanding the release media is important. A related suggestion was the concept of quantifying silver nanoparticle half-life.

Finally, it was questioned if the scope of the NanoRelease Project included silver released as ionic species, or only silver released as nanoparticles.

MWCNTs

Participants agreed that release of free (unbounded) MWCNT from a polymer-based product containing MWCNTs was unlikely. Rather, the released "entity" would be a piece of the polymer matrix with embedded MWCNTs sticking out of the piece. Participants agreed that a flux measurement was important and felt that release should be measured using a two-step approach:

1. Is there a release of polymer-MWCNT entities into a medium? A proposed basic degree of release is: [total mass of MWCNTs released or total mass of the released entities]/total mass of the product]
2. If so, perform follow-on studies to evaluate polymer-MWCNT entity release with time

The participants agreed that the most likely release mechanisms were long-term degradation of the product due to wear or weathering, and catastrophic release by mechanical means, *e.g.,* crushing by impact.

There was discussion among participants in both groups that no single technique was sufficient for analysis of MWCNTs. Currently available measurement methods include:

1. FT-IR
2. Raman spectroscopy (for SWCNT only?)

A MWCNT release expert in the first group commented that methods to quantify the release of MWCNTs are not sufficiently well-developed to support a release study.

A MWCNT release expert in the second group commented that sample collection methods for drilling and sanding operations are ready to be "standardized".

Detailed Notes by Presentation and Additional Notes from Invited Experts

DAY 1

Introduction and Charge to Participants

- The SC needs guidance from the experts, what would be best to look at – but we also need to be practical in the context of uses, and what's practical for us to understand.
- In addition to the likely exposure scenarios, there are susceptible populations.
- In terms of methods – the SC doesn't want to reinvent the wheel, if a method is available, we may need to increase the confidence in that method(s).
- One thing the field needs is be able to link hazard data with the release methods / data in the hope that this will be informative for risk assessment.
- From an industrial perspective: we need methods that are available to companies and industries and, at best, the tools/methods needed are not too expensive.
    - Another aspect to follow-up on the previous, we should also keep in mind the limitations of the tools available. One possible approach could be to increase released material concentration.
- In acidic environments, there's a lot of release of CNTs. And higher level of release for n-SiO2 with higher stresses (e.g. force, speed)

Handling Confidential Business Information (CBI)

- Take away – it will be a challenge and will require some creative thinking – but it is possible and should not be viewed as a stumbling block.
- Use a 3rd party that understands CBI methods – serves to collect / process info / and readout sanitized data.
- When testing is done, decisions will need to be made on which material (i.e. whose) and how will it be packaged (double blind) or blend commercially available materials with non-commercially available.
- Sharing analytical methods – this might be some of the most difficult to do. Again, it should be doable, through a 3rd party, randomize the methods and materials being tested.
- Need a nondisclosure agreement set up among the 3rd party, any companies and labs involved.
- EPA has been collecting CBI filings since the 1970's. EPA has been successful through the use of policies, regulations and laws – which could be useful models/guidelines as you develop a process under the NR project.
- Perhaps the best example now is "RADnet"?? monitoring radiation leakage from Japan. But EPA uses ePMNs with software packages. There are other internet applications / cloud based networking (e.g. CDX, REACH) and from IBM, Microsoft, google… "online secure collaboration platforms"

Question: Does the NR SC intend to post interim data on the internet? Answer; the state of the science, the methods to be tested – yes. However, there will be CBI, or at the least, sensitive and we will have to be very careful to prevent from that information from being disclosed.

- The composite materials in existence, there's a limited number of suppliers. Because of these limitations, the final report(s) despite sanitizing, it will likely be able to figure out what was used. – participation is vol. And, another approach would be to have a 3rd party develop a material in collaboration with a company that produces something that's representative of commercial products, but is not a product, and would not likely be a product.
- There's also the possibility that a proprietary analytical method may go through the round robin testing, and be identified as the best one. In this situation, there will likely need to be disclosure at some point.

NANO-SILVER PANEL

First Panelist: **Najim Shamim**, EPA/OPP -- n-Ag in pesticides, under FIFRA

- OPP PMNs – highest volume submissions: non-food contact textiles & polymers preservative, algecide in swimming pools, dental waterline cleaning, hard surface disinfectants
- EPA-SAP – (size advisory panel) held in 2009, and posted on the web
- EPA-OPP is attempting to model exposure, and also asks for submission of models based estimates of exposure with the submission. – however, these are not public. So, in some cases we are receiving some release data, and it's clear that release rates different among various substrates.

Second Panelist: **Murray Height**, HeiQ -- Nano-silver in textiles

- Many silver types that can be used for antistatic and antimicrobial properties – nano-silver represents a minor part (<25% of the anti-microbial textile market)
- The mechanism of action always comes back to the *silver ions*, and not NP of silver themselves.

There are three broad categories of silver used in textiles:

(1) Silver ions exchanges – developed in Japan in the 1970s, is the most extensively used and has the greatest Ag+ release potential (e.g. $AgNO_2$).
(2) Metallic silver – used extensively, but has the lowest Ag+ release potential (e.g. Ag_2S).
(3) Silver salts – developed very recently, which releases Ag+ at a moderate rate and amount; therefore, the best to use in textiles is high-surface area silver (typically nanoscale) and AgCl.

During textile manufacture, there are three opportunities to add nano-silver:

(1) Master-batch – (spun into fiber) often requires higher level of loading, but also lasts longer and has better durability
(2) Finish-line – (captured in a film or polymer coating) lower level of silver needed, long durability
(3) Misc - (surface deposition) doesn't work as well, poor durability and thus not typically used.

Known silver/textile release scenarios:

Ions – yes, all production methods do, as that's the intention
Nanoparticles – yes, from misc production methods (e.g. Benn et al 2008 and Geranio et al 2010)

Recommendations to the SC: (1) ensure realistic conditions are used to induce release and (2) conventional commercial products are tested along-side n-Ag textile.

Third Panelist: **JoAnne Shatkin**, CLF Ventures -- Life Cycle Considerations

- To date, there has not been much consideration of primary and secondary contamination from release nanomaterials
- There are a diversity of sources to consider - fabric thread count, type and application process

Fourth Panelist: **Bernd Nowack**, EMPA -- Modeling n-Ag release in the environment

- The release "profile" of n-Ag from textiles in pH10 vs washing machine is dramatically different – but we do not know if these differences are dependent upon the analytical tools we used.
- In washing fluid – almost NO detectable dissolved silver.
- Matrix dependent release characteristics
- The form of released silver is largely unknown

Fifth Panelist: **Rob MacCuspie**, NIST -- Measurement challenges for n-Ag

- No standard for stock solutions
- The timing is very important as Ag NP stability varies dramatically
- Detailed reporting is critical – but often lacking

Recommendations to SC:

- Need intensive initial characterization
- Routine screening
- Use relevant conditions and time frame
- Please report the "trivial" and "obvious" data, it's helpful

Ncl.cancer.gov is the NIST assay cascade protocols website – good source

Questions for n-Ag panel

(1) Transformations immediately after release, to chloride or sulfide – how rapidly does this occur? In other words, when does the source term stop?

- If transformation is a surface driven, the smaller the particle = faster transformation. There's also UV induced transformations – and again it appears that smaller particles transform more rapidly.
- EWAG has seen n-AgCl to n-AgS fairly quickly. And there's evidence that AgCl will be most common. – so, speciation may be more important to examine then transformation.
- The Westerhof group has a paper in prep on nanoparticles 60-80% of silver released remain within the interface.

(2) Since the textile matrix has such an impact on release, do the conditions (sweat vs. washing) have equally dramatic impacts?

- The Holinstein Inst in Germany looked at n-Ag in textile on skin, release due to contact and possibly sweat, but didn't report significant findings.
- The washing cycle is, by far, the harshest conditions that a textile will encounter during its life cycle. After washing, there's rinsing and then subsequent wearing/sweat, and over time perhaps the 'worst' scenario could be wearing a textile without washing it from the store.

(3) What's the likelihood of NR project success using n-Ag?

- Bernd - It would probably be easier to work with something that you don't have all these reactions and speciation issues. Because the form of the silver is very important.
- JoAnne – speciation definitely adds a layer of complexity. If we are only interested in release, and not the form (which really gets to hazard), then silver may not be too difficult, but we will have to consider the difficulties posed by measuring all the different released forms.

MWCNT PANEL

First Panelist: **Laurence Libelo**, EPA/OPPT -- nanomaterials under TSCA

- OPPT has received roughly 110 submissions of new "nano" chemicals, about 50% are MWCNTs in polymers
- OPPT makes several assumptions and relies on models, but until we have better data, we can't make better models.
- Our models are typically based on organic compounds, and solubility characteristics for bulks materials.
- EPA/OPPT is still trying to figure out what a "worse case" would be for nanoparticles.

Second Panelist: **Jackie Issacs**, Northeastern University -- Life Cycle Considerations

- End of life is a critical step – recycling, incineration, repurposed, landfill, etc….
- CNT polymer mesh, used in EMI shielding, switches – may be good carrier systems to use.
- Nanocomp – CNT sheets for military shielding.

Question: The differences between SWCNTs and MWCNTs was raised in terms of uses, would it be reasonable to expect that they have different release and/or degradation?

Answer: Yes, but we don't really have good data on this. Most data come from incineration studies.

Third Panelist: **Ray David**, BASF

- Higher number of particle release from harder materials, but it appears that these particles were not the cement, but rather were artifacts.

- Weathering – particles are released from polymers, but these are larger then the n-SiO2 embedded into the matrix. It appears the polymer degrades away, and thus nanoparticles are released.
- Weathering or chalking appear to be the most important life cycle stages.

Question: The weathering study looked at UV, but what about moisture, etc? Answer: They only looked at UV, so we don't have data.

Fourth Panelist: **Gwen Gross**, Boeing Company -- Life cycle and Initial Characterization

- Considerable interest in recycling carbon fibers, as they are expensive – go into bike frame, plates, trays, seats, etc. recycling through chemical dissolution, which likely makes CNT sludge during the recycling process.
- A "clean room" type environment for airplane production is not realistic. So, what type of capture is necessary, but only do able if we know where/when there is release.

Boeing did a small study with a MWCNT composite panel -- considered sanding, drilling and grinding. Chose to go with sanding.

- Boeing, UW (Mike Yost), Battelle Lab group
- Epoxy resin carbon fiber composite panel with ~1% MWCNT (w/w resin)
- Background concerns paramount
- Used Raman scattering
- Generated a lot of NP in 20-40nm size range, which is too small for MWCNT.
- Going back to the composite, the curing of it with the MWCNT altered the MWCNT size/structure.
- Did not find an unbound CNTs, but did find a lot of polymers with CNTs embedded.
- No significant agglomeration observed

Take away from the study:

(1) the multi-disciplinary approach is necessary, but it's also a big challenge to bring the groups together, and communicate scientifically.
(2) TEM is not a good method for use in real work / shop floor settings. No knowledge of background, and historically present vs novel.
(3) toxicology is so focused on initial production and not on end use, or consumer uses, that we really need the links.

Fifth Panelist: **Dhimiter. Bello**, Umass/Lowell -- Machining of hybrid composites w/CNTs

- CPC and TP/ESP are perhaps the best tools (cheap and effective for aerosolized particles) – but do we miss other important data? i.e. what is shown by TEM, which is very limiting.
- Size, chemistry and morphology are probably the most important variables to measure.
- Let the engineers define the scenarios for release based on their actual uses/manipulation

- It would be best if the SC designed the experiments to collect data within established conceptual frameworks.
- Nano-ropes, the bending of CNTs and bundling appears to reduce structure integrity.
- One thing the field needs is a standard method of sampling and reporting statically useful TEM data.

Personal note: why isn't a sampling grid and random # process used like in *in vitro* cell counting??

Questions for the MWCNT Panel

(1) The metals listed in the various MWCNT – are these metal oxides or native metals?

- Not known, but it appears most are metal oxides with the exception of Cr.

(2) Does the panel think it would be easier to work with CNTs compared to n-Ag?

- Bello – silver would be far easier, although it is complex itself. There's such a wide range of CNTs, which would be necessary to characterize.
- Gross – based on the Boeing study, it's clear the MWCNT characterization is necessary because its incorporation altered both the carrier system and the MWCNT itself.

(3) To follow up on Gwen's comment: It appears the n-Ag changes through the life cycle (the speciation of silver is a moving target). Meanwhile, the CNTs change when they are put into the matrix and then remain that way – is that correct?

- Not entirely, but it's not really known. However, most of the complexity comes from the wide range of CNTs.

(4) Textiles seem to be a wide range of products, what about CNTs?

- Yes, the CNTs are used - widely in polymers of sporting goods, auto industry. Wind turbines would likely be next and then the aero-industry.
- A commonly used polymer matrix: diglycidyl ether bisphenol A (DGEBA) based with amine curative (dicy, DDS) + carbon fibers (MWCNT)
    - Sporting goods, auto industry, wind farms, aerospace composites
    - Other curatives include anhydrides but they are more chemically unstable (hydrolysis), but are cheaper so may be used
    - BASF has some products in these types of chemistries as well as other companies"

Comments from the audience:

- It should also be kept in mind the chemical dynamics of functionalized CNTs, as release occurs, does it do so in a manner that exposes the internal chemistry?
- Perhaps most important is to keep in mind the need for a baseline. Have nanoparticles always been released?
- Is there a correlation between doping with nanoparticles and release of nanoparticles?
- Material (polymer) repair is a worthwhile exposure scenario.

DAY 2
STANDARDS PANEL

First Panelist: Robert Cook, NIST

- When thinking of methods to standardize, broadly you're looking at: exposure, sampling and content measurement (i.e. size, shape, particle concentration, etc).
- The field is moving quickly, and probably has the best handle on measurement standards – they need to be better, but there's a good start.
- 900 measurement standards for EHS - -what we need now, is measurement for nano, and for nano in products.
- NIST & BAM (Germany) – 65 nanoscale reference materials, of these 15 reference materials relevant for EHS
- NIST-CEINT and NIST-NCL have also developed protocols

Case study for n-Au – standardized characterization
Assay took about 1 yr.
Ref material production -- 2yrs
Documentary standard development/interlaboratory testing – 18mo
TOTAL process: 4.5 yrs

- Later this year, NIST plans to finalize/release nanoparticle ref materials for SWCNTs and n-Ag.
- When measuring size, the method used induces a bias and that bias is greater when measuring smaller particles (i.e. 10nm = little agreement among methods. 60nm = full agreement among the same methods)

Second Panelist: Richard Holbrook, NIST

- Developed a "wet-TEM" method to examine nanoparticles
- Donnan membrane technique - to measure amount of Ag ions from n-Ag in solution.
- In our experience, particle transformation occurs naturally and often rapidly.
- A question the field is struggling with is, what's more important for release rates, mass or particle number??
- We used a "Fractional factorial" study design to obtain a more robust data set.

Recommendation for the SC: Materials conditions and measurement would be the best areas to focus for increasing understanding for release

Third Panelist: Alex Stefaniak, NIST

- No sampling technique exists that specifically identifies/measures engineered nanomaterials vs. natural or accidental
- Lack of validation for the instruments – and based on assumptions that NP are smooth spheres (which we know they aren't)
- Comparability of instruments is unknown
- "off-line" analytical techniques can be specific and helpful in subsequent particle characterization.

Fourth Panelist: Tinh Nguyen, NIST

- Release of n-Si appears to occur, and can be modeled using 1st order reaction kinetics.
- Polymer composite surface degradation due to UV exposure happens very quickly (~15min), but it takes a very long time/high UV intensity to degrade into depth of the composite.
- One problem is the differences in instrumentation (e.g. age, maintains, etc) in the various labs used in the interlab testing phase. -- doing comparisons among the labs' testing on standard ref materials.
- A good approach is to use 2-3 labs first, and then do the full testing.

Questions for the Standards Panel

(1) What are likely to be "low hanging" fruit from a test method standpoint?

- Want to be sure to normalize the release back to the initial conc.
- Sunlight and UV are good
- There's also a minimal level of tools required (i.e. TEM) for the studies to be robust and of high value.
- One good approach for the project would be to begin with the best tools, and then compare cheaper tools to find ones that could be used to still obtain the data.
- For the SC to consider: -- there are two competing interests, the complexity of the material side, or the detection side.
    - Material complexity – n-Ag more complex and changes over time, CNTs are stable after release
    - Detection: far better methods to detect n-Ag, and poor methods for CNTs.

(2) Much of the discussion has focused on abiotic degradation/release – has anyone looked at biotic degradation? -- Alex Star's group has

(3) Is there a good candidate for developing a representative material / and release measurement method?

- R. Cook – recommends exploring n-Ag.
- B. Nowack – recommends exploring n-TiO2 b/c you can avoid speciation issues, the release pathways are better know (sunscreen), or in paints – thus eliminating a number of the complications associated with Ag or CNTs.

Additional general comments from Kim Rogers
1a It appeared from the presentations and discussions that several issues seemed to surface.

Although exposure and potential effects were not the main focus of the workshop, it seems that carbon nanotubes (SWCNT, MWCNT) may present problems in a work-place setting (manufacture, polymer formulation and modifications – grinding, drilling, etc.). Exposure issues for nanosilver (all forms metal, metal oxide/chloride, etc) in fabrics may involve not only manufacture/garment fabrication but also normal use and extended use by consumers. In addition, nanosilver fabrics may also involve exposure to susceptible populations (e.g., children).

1b In terms of material/matrix, I believe that I was hearing from the group that CNTs would be very difficult to measure when released from polymers in real world scenarios. By contrast the analysis of total silver release would be fairly easy to measure using commonly available instrumentation. Characterization of its form; however, would be possible but more challenging. Given that the steering committee's charge seemed to involve completing this project within a fairly short time-frame, it is my opinion that silver release from fabric (potentially multiple manufacturers) would be the most feasible option (at least for the initial project).

1c The "low hanging fruit" option might involve an observational release protocol (observational because you will not really know what you are being presented with from multiple manufacturers – various fabrics, immobilization methods and forms of silver).

It was mentioned that solubility is a key issue for release of silver ion. Because the composition of the release/leaching media (i.e., presence of chloride, sulfide, pH, etc.) will essentially determine the solubility of silver ion, I would suggest using both pristine and real-world release matrices followed by total silver analysis and then separation/characterization protocols to determine the presence and composition of potentially released nanoparticles. This strategy should be able to measure the release of ions or particles as well as the possibility of in-situ formation of particles from released ions.

Additional comment from Troy Benn on n-Ag
I would offer another plug for using a simple analytical method for silver detection. That is, sequential filtration (450 nm, 100nm, etc.) and subsequent total silver quantification with ICP-MS or OES.

This method is simple enough that I would imagine you could get very similar results between labs, and the materials would be fairly cheap. I think it would be very easy to convince the consumer product industry to participate, if they aren't doing something similar already. It might be interesting to add a "laboratory" that isn't from academia. It would also allow the testing of different release solutions, as it seems many people were interested in the difference between water, wash-water, sweat, or saliva. Testing

different solutions might tell you what environments are likely to see more (nano)silver release.

I hope this is useful. Thanks again for the opportunity to participate. When the committee narrows down the focus/goals of the project, I think another round of discussions with the analytical chemistry academics will help with designing protocols.