

Tamper-Indicating Enclosures with Visually Obvious Tamper Response

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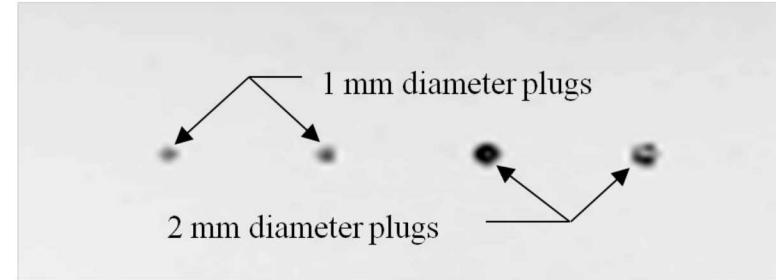
Project Objectives

- Improve tamper-indicating enclosures (TIEs) by making response to tamper obvious through simple visual inspection
- Material dramatically changes color irreversibly upon tamper
- Adversary cannot repair or hide tamper-attempts on material
- Material is robust to environment and facility handling
- Material can be 3D printed, or applied by paint or spray coating to existing surfaces
- Material is low cost and deployable across wide range of applications
- Material facilitates rapid and objective inspection

Background

- Current TIEs either need time consuming and subjective inspection, active monitoring technology, or external verification mechanisms. There are no approaches that upon tamper, result in obvious responses with only visual inspection needed.

Example of Current TIEs

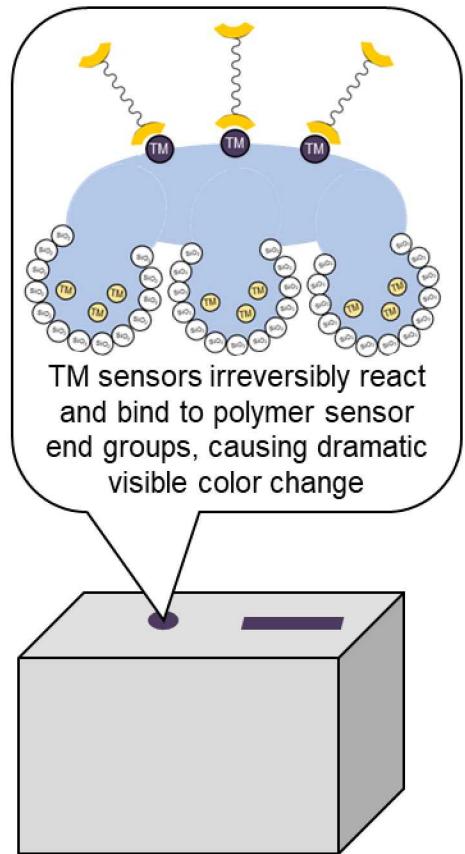
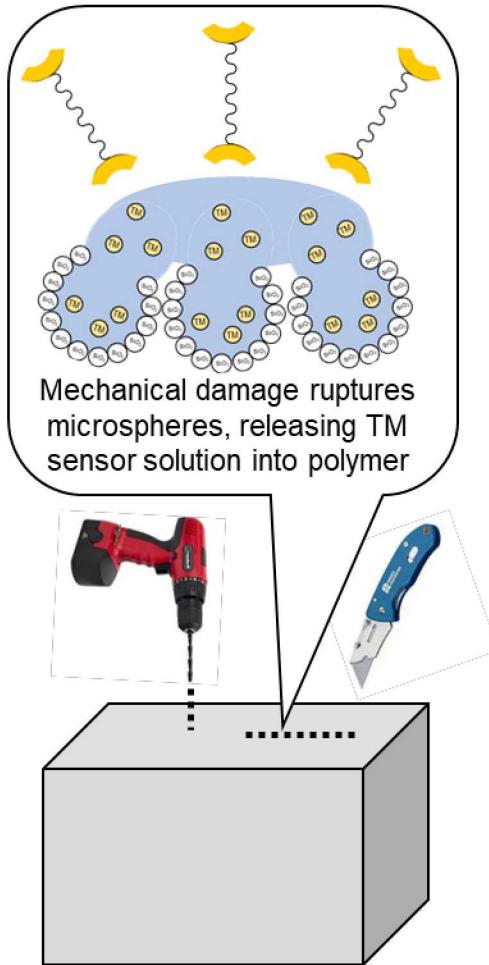
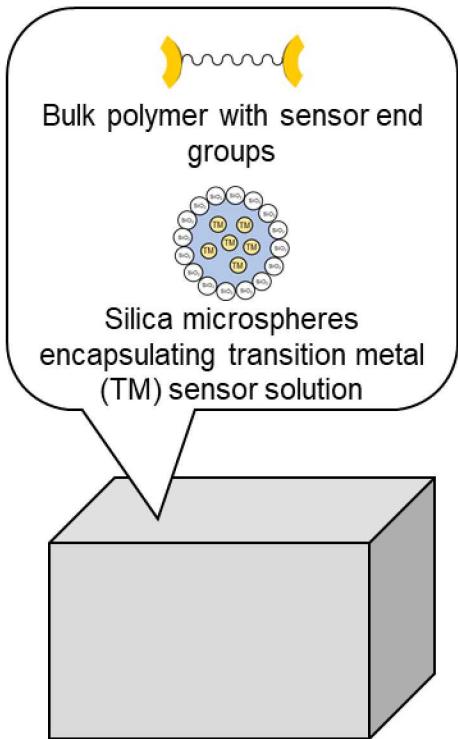


(Left) NGSS surveillance system uses both anodized aluminum, which is verified subjectively on both the outer and inner surfaces via visual inspection and touch, as well as active self-monitoring using conductive materials. (Middle) The EOSS fiber loop seal uses active self-monitoring using conductive foils. Active methods require power and are not applicable in some scenarios. (Right) Metal containers can be verified using eddy current – an external electronic instrument capable of finding disturbances in the metal, including drilled and plugged holes.

Approach

- Design and develop microspheres that will contain desired cargo.
- Optimize microspheres in terms of wall thickness, size, permeability, and force required for rupture, and integrate the microspheres into 3D printed and spray coated geometries.
- In parallel, design and develop cargo that causes permanent and obvious color change in response to ruptured microsphere.
- Develop prototypes which will undergo testing and evaluation, including environmental and industrial handling.

Concept



Microspheres progress

- Silica microspheres containing Cu^{2+} and Fe^{3+} (transition metals) successfully synthesized by an acid catalyzed SiO_2 condensation in a water-in-oil emulsion
- Size distribution of spheres \sim trimodal 0.5 - 1, 2 - 5, 10 μm
 - Shell thickness $\sim 1 \mu\text{m}$
 - Rupture attempts by grinding between two glass slides unsuccessful – need to mitigate
 - May need to increase sphere size for more facile rupture
- Microsphere core contents easily extracted with hydrophilic solvents (e.g. EtOH)
- Silica shell contains micro- and meso-pores (is permeable) – currently exploring strategies to mitigate

Acid catalyzed SiO_2 condensation



magnetic
bottle



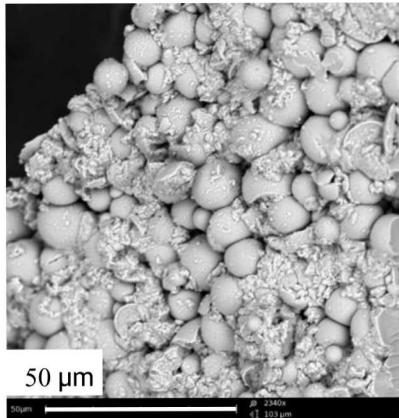
magnetic
jar



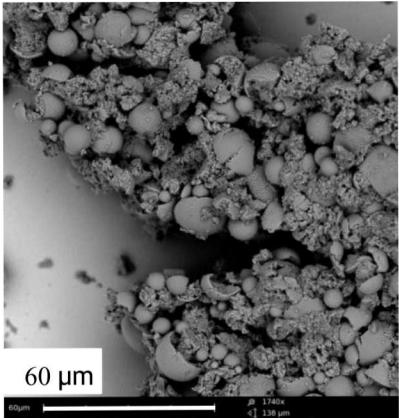
overhead paddle
round bottom



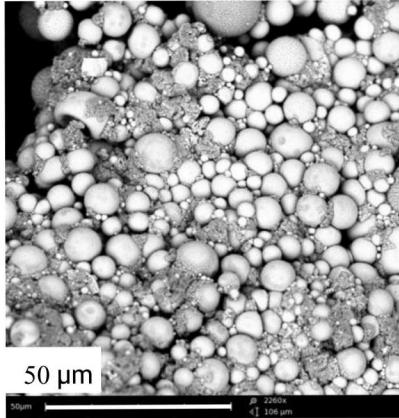
overhead propeller
plastic bottle



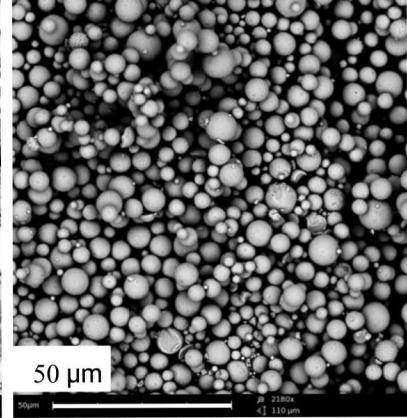
debris



debris



less debris

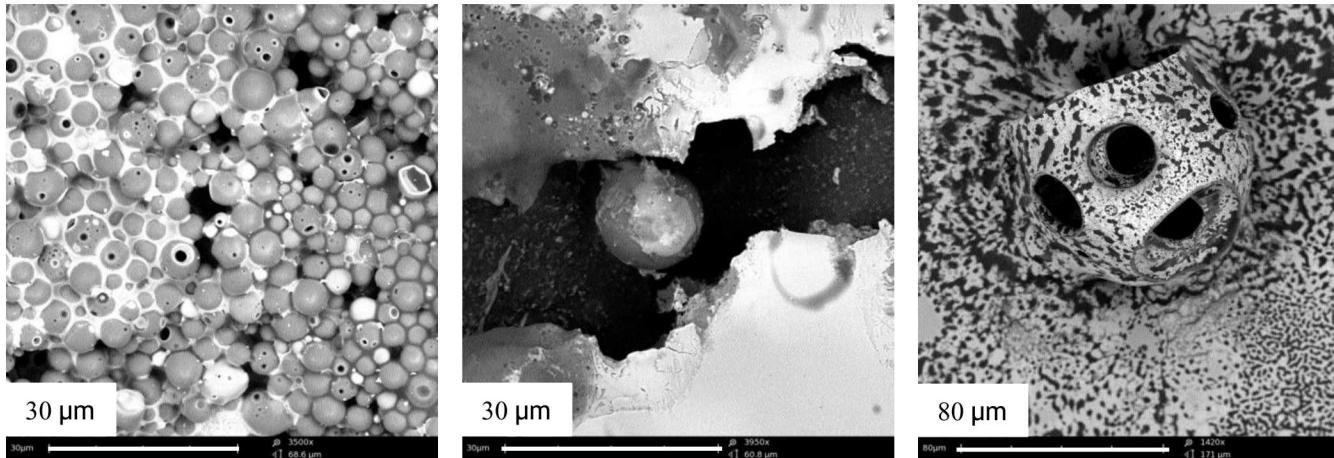


clean

Composite microsphere approach

Concept: polymer inner sphere to control capsule permeability, silica outer shell to impart structural rigidity

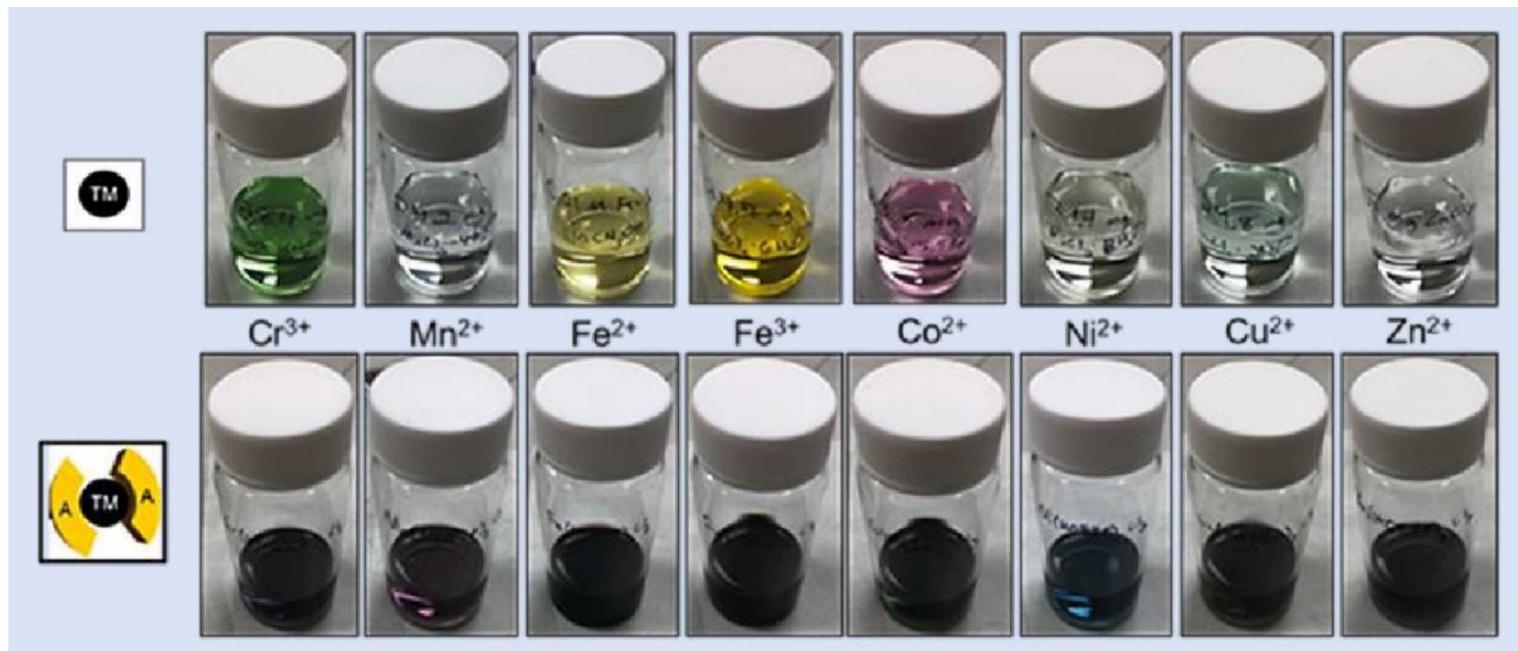
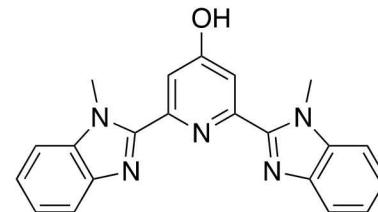
- Initial system: Polyvinyl alcohol / silica
 - Multiple synthesis attempts unsuccessful
 - Silica does not seem to be evenly coating the polymer spheres



- Poly (acrylamide) / silica will be attempted
 - Evidence for success in literature

Sensor compounds (Metal)

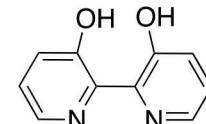
Screening study performed on various metals with below organic sensor.
Need both color change and optimal sensor/polymer interaction



Sensor compounds (Organics)



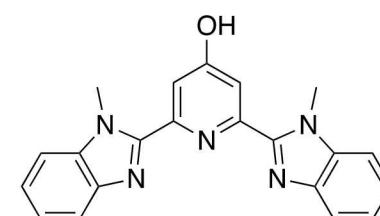
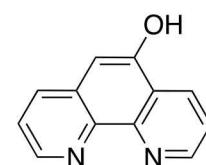
Sensor compound in solution



Fe(II) + Sensor

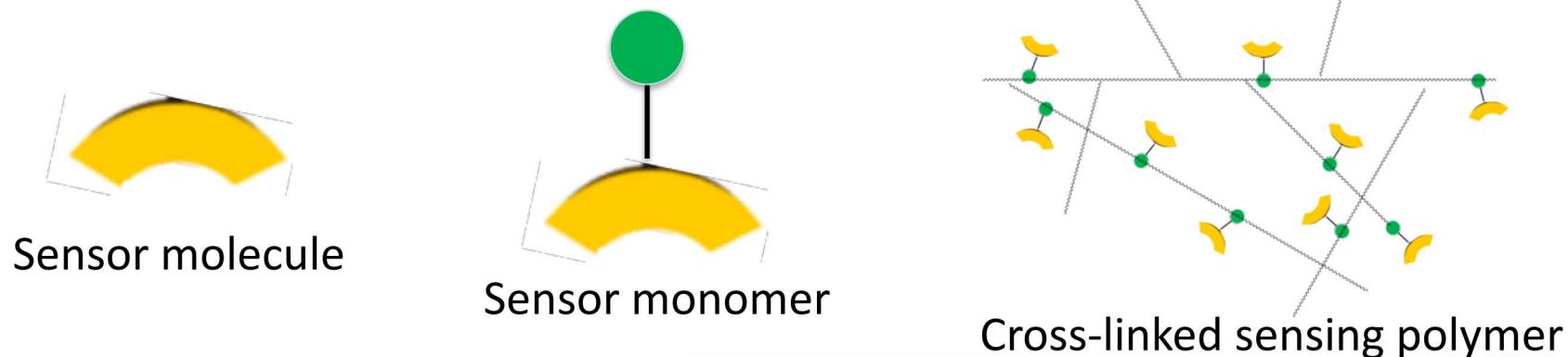


- Fe(II) – Pale yellow solution
- Sensor compounds
 - Colorless solution
- Addition of Fe(II)
 - Dramatic color change!
 - Very little material required

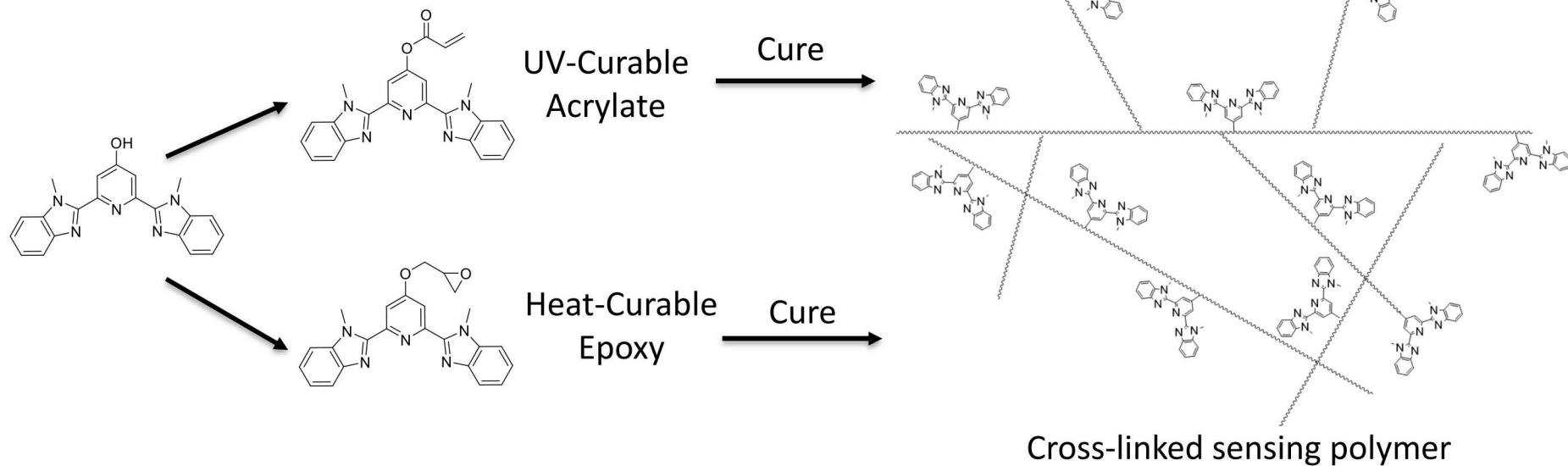


Sensor Incorporation into Polymers

General schematic



Detailed schematic



Next steps

Microspheres

- Pure silica system – explore synthesis strategies to block wall pores and control permeability
- Polymer / silica composite system – explore poly (acrylamide) / SiO_2 synthesis

Sensor Compounds

- Investigate various metals: Fe^{2+} , Fe^{3+} , Mn^{3+} , Co^{2+} , Co^{3+} , Cu^{2+}
- Determine the reversibility of metal-sensor interaction
- Investigate methods for sensor compound incorporation
 - UV-curable (spray-coatable or 3D-printable) and thermosetting epoxies (poured into enclosure moldes)
 - Polymerize from sensor compounds