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Synthesis and Characterization of Smart Functional Coatings by Chemical Solution Deposition Methods

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ABSTRACT

New coating technology enables the fabrication of low cost structural health monitoring (SHM) and tamper indication devices that can be employed to strengthen national and international safeguards objectives. In particular, such innovations could serve the safeguards community by improving both the timeliness of detection and confidence in verification and monitoring. This work investigates the synthesis of functional surface coatings using chemical solutions deposition methods. Chemical solution deposition has recently received attention in the materials research community due to its unique advantages such as low temperature processing, high homogeneity of final products and the ability to fabricate materials with controlled surface properties and pore structures. The synthesis of functional coatings aimed at modifying the materials conductivity and optical properties was investigated by the incorporation of transition element (e.g. Cr^{+3}) and rare earth (e.g. Er^{+3}) serving as dopants in a polymer or gel matrix. The structural and morphological investigation of the as-deposited films was carried out using UV/Vis and photoluminescence (PL) spectroscopy. The as deposited coating was further investigated by scanning electron microscopy and energy dispersive x-ray microscopy.

INTRODUCTION

The DOE/NNSA and IAEA has recognized the need for the development and implementation of advanced authentication, verification, and **unique identification (UID)** schemes for international safeguards applications. One of the areas of need is the development of a new generation of intrinsically tamper indicating ceramic seals (ITICS) that can replace a metal cup seal used by the international safeguard community.
Seals are used in nuclear verification regimes in order to ascertain if material has been introduced or removed from a tamper-indicating container or that unattended monitoring equipment has not been altered. Additionally, seals provide a unique identity (a tag) for the sealed container or item. Seal criteria include reliability, tamper-indication, in-situ verification to reduce inspection effort, ease of evaluation of results, high level of conclusiveness, and ease of use. Researchers at Savannah River National Laboratory (SRNL) and Sandia National Laboratory are collaborating in the investigation, evaluation and integration of synthesis functionalized polymers and coatings for authentication and verification of ceramics seals. The main goal of this project is to enhance detection capabilities and verification schemes through the development of smart coatings.

SMART COATINGS

A smart coating is a system that can function as a sensor or actuator by responding to physical, chemical, or mechanical stimuli. Changes in properties and structure, in response to changes in the environment can then be verified by a readable signal. Integration of functional materials to polymeric coatings is a powerful tool for producing smart materials that combine several properties and may respond to external conditions. Smart materials are expected to be used not only as a passive materials barrier but also as an integral part of complete smart structures composed of various elements including sensors, actuators, control algorithms, control hardware, and structural members. Some of the benefits of smart coatings include; 1- capabilities to respond to physical, chemical or mechanical stimuli by developing readable signals, 2- changes in properties and structure, in response to change in the environment, are in many cases reversible, 3 Responses may often actuate, in addition to simple sensing, corrective action such as self-mending or healing.

SAFEGUARDS APPLICATION

Containment verification and remote and unattended monitoring is a high priority for safeguards. Nuclear material containers, equipment cabinets, camera housing, and detector cable conduits are all vulnerable to tampering or counterfeiting when fielded. In many cases it is very difficult to distinguish them from genuine products. It is in these aspects that smart coatings can provide a layer of protection to the surface and increase the defense in depth by sensing other parameters that would allow the inspector to uniquely identify the item in-situ and extract information that can be used for continuity-of-knowledge and information driven safeguards. Advantages of smart coating include;

- Can be incorporated into almost any surface,
- Can be functionalized for enhanced safeguards, verification and monitoring
- Non intrusive methodology for UID
- Can be modified for process or facility specific applications
- Cheap and easy to use by inspectors

Research in the polymeric coatings can provide in-situ information for monitoring and verification of the health of a system that can simplify field inspections by incorporating in-situ readings that can quickly reveal an illicit attempt to modify, intrude, or illegally divert safeguarded material

METHODOLOGY

Fluorescent coating research is being performed in support of synthesis and development of fluorescent seal coatings. Synthesis of fluorescent functional coatings by chemical solution deposition methods based on silica gel (tetra ethyl orthosilica TEOS) has been performed to incorporate fluorescent species to the surfaces of ceramic specimens. It is shown in figure 1 the approach followed for the synthesis and thin films deposition of smart coatings in specimens of interest (e.g. ceramic surface). R&D work on this task has been focused on the methodology to prepare coatings with fluorescent centers. Different ionic dopants based on rare earth and transition metals (e.g. Er^{+3} and Cr^{+3}) have

been identified. These dopants will be incorporated in sol gel matrix that can be utilized for thin film deposition. Techniques for deposition of the sol-gels on ceramics are currently being developed. Once the deposition techniques of the fluorescent coatings are determined, research will begin on application of multi-dopant conductive and fluorescent coatings.

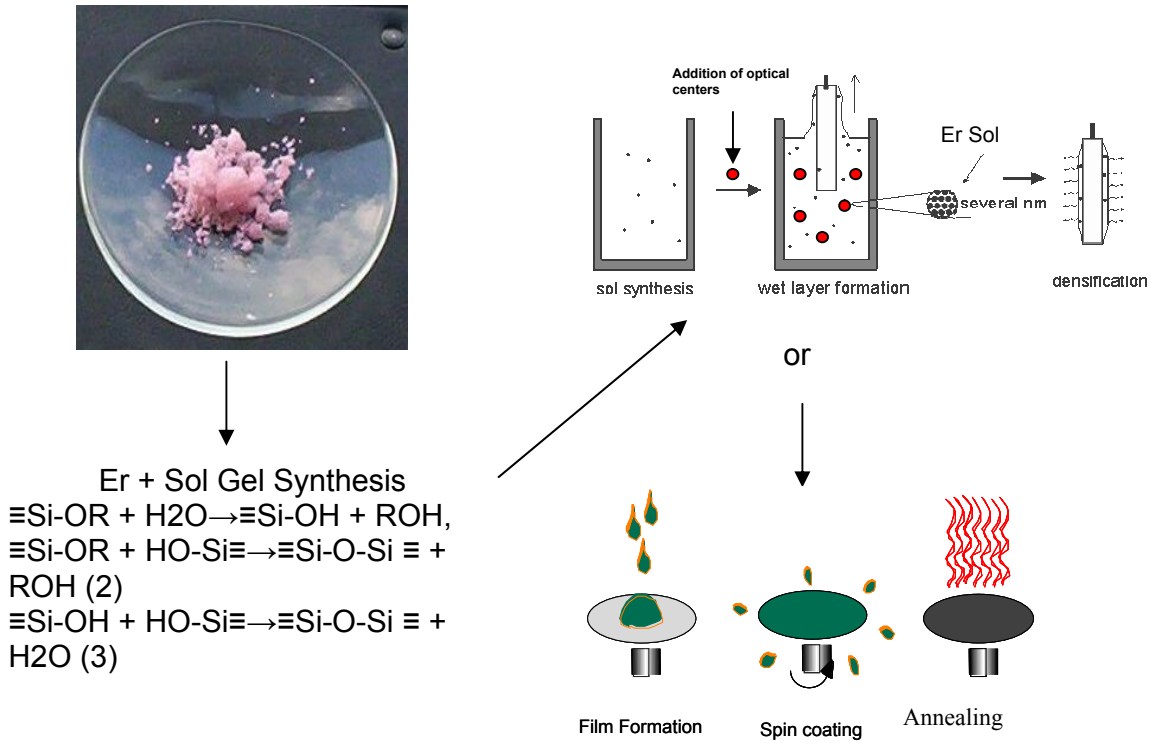


FIGURE 1. Synthesis, functionalization, and deposition of smart coatings

The smart functionality will be imparted by functional additives added separately into the polymer or coating prior to its application on a given substrate or be built in the polymeric structure as conceptually shown in Figure 2. Table I summarizes the characteristics of selected optical centers with their described absorption and emission wavelength used in this study.

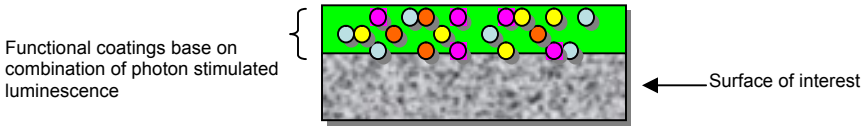


FIGURE 2. Smart conductive and polymeric layered system with functional materials that combine several intrinsic properties and may respond to external conditions.

TABLE I. Functional additives with absorption, emission and excitation regions.

PSL precursor	Absorbs in	Emits in	λ_{ex} (nm)	λ_{em} (nm)
Coumarin	UV, Visible	UV, Visible	459 370	520 490, 610
Chromium	UV, Visble	UV, Visible	390	483
Erbium	UV, Visible, IR	UV, Visible	377 488 520	426 575 617
Neodymium	UV,Visible, IR	UV, Visible	290	365, 401
Samarium	UV, Visible	UV, Visible	294 380 460	356, 385, 413, 430 430, 563, 597, 644 507, 562, 597, 644
Terbium	UV	Visible	350	493, 539, 555, 585, 623

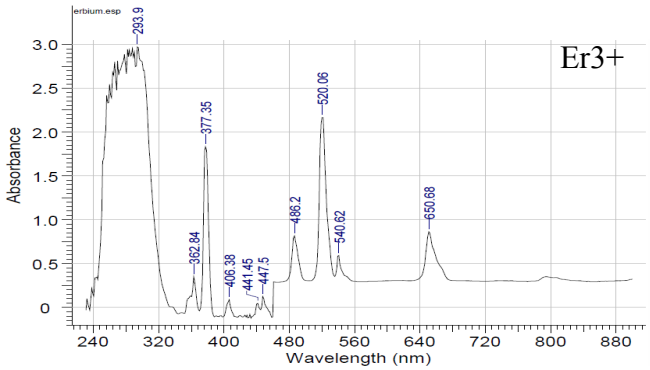
RESULTS

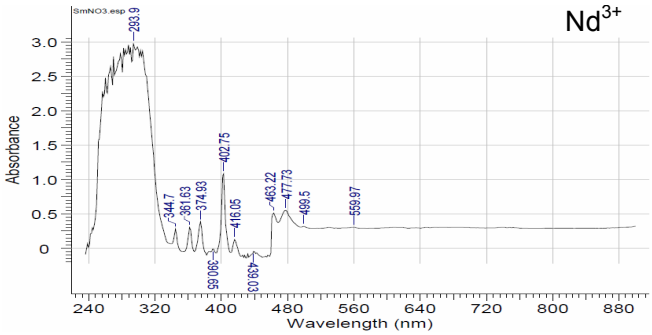
UV-Vis

For UV-Vis absorbance measurements (Si Photonics 4100), a deuterium (UV excitation) and tungsten (visible excitation) source is used to study the absorption and transmission spectra (250 – 900nm). All the samples (either solution or sol-gel form) were placed in cuvettes so their optical centers could be excited. Absorption spectra of selected ions are shown in figure 3 (A-D). UV-Vis Absorptions and transmission were performed on TEOS to study the transparency and absorption characteristics of the non-functionalized gel matrix. It was observed high degree of transparency (<90% transmission) on the gel solution.

Photoluminescence Measurements

For photoluminescence measurements (JY FluoroMax-4), a xenon light source is used to \excite the samples in the UV region (260 – 390 nm). All the samples (either solution or sol-gel form) were placed in cuvettes so their optical centers could be excited. All the rare earth compou s, when excited in the UV, emit light in the visible region (400 – 650 nm). Each spectra was record with a 0.5 second integration time per 1 nm intervals. Figure 4 (a-d) show photoluminescence spectrum for selected excitation.





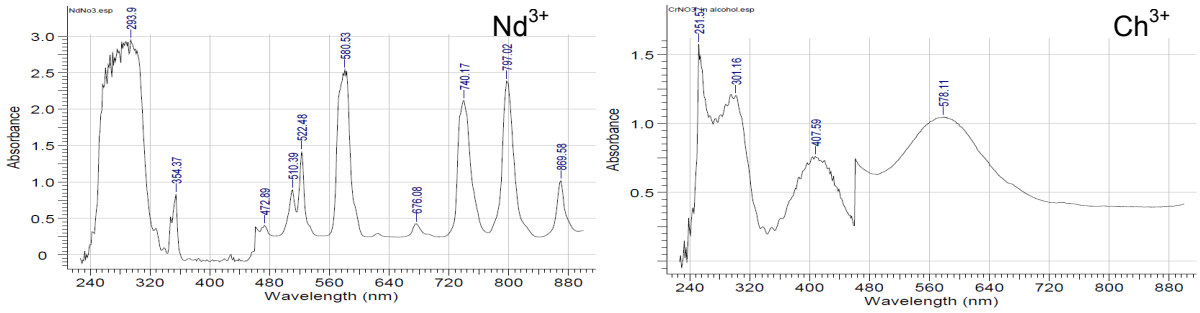


FIGURE 3. (A-D) Absorption spectra from Er, Sm, Nd, Cr

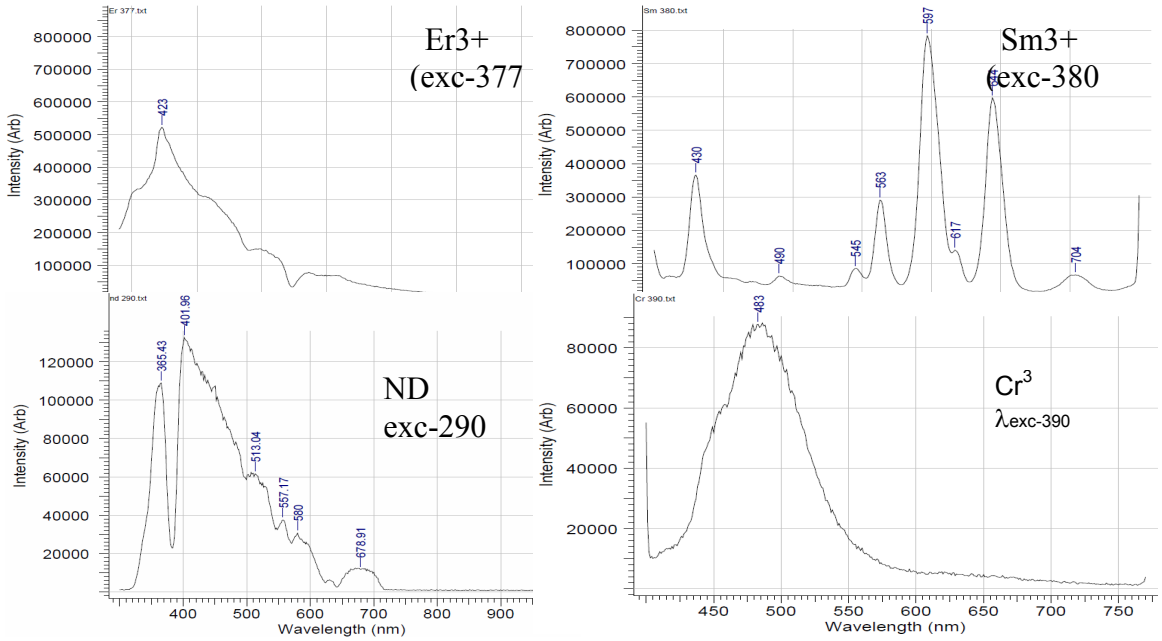
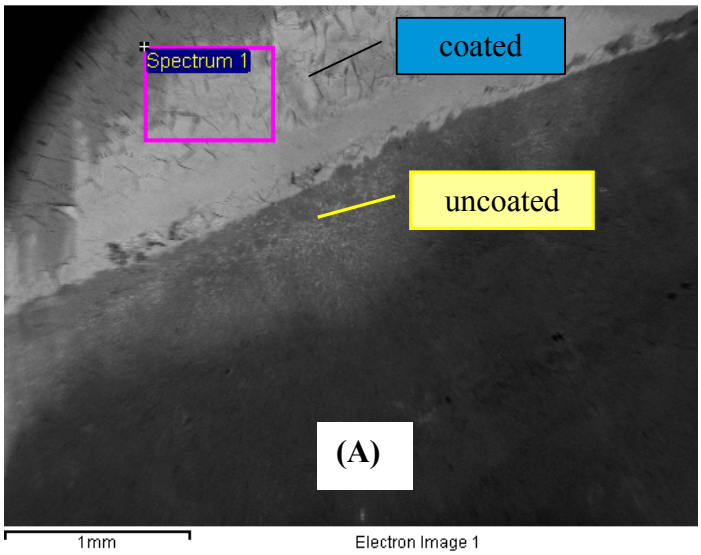
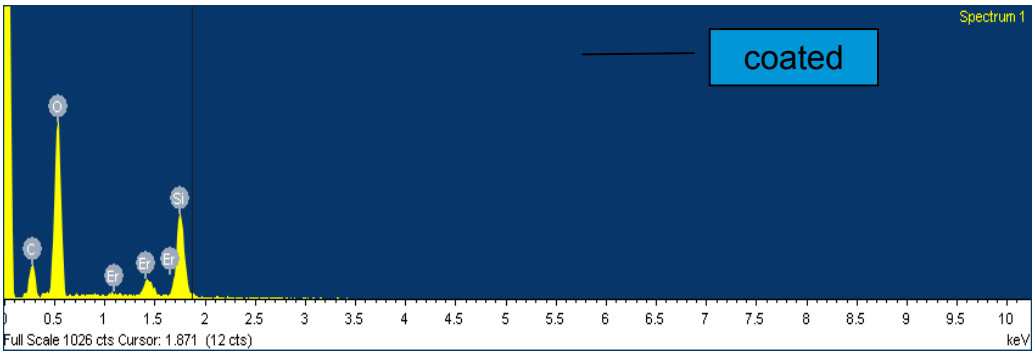
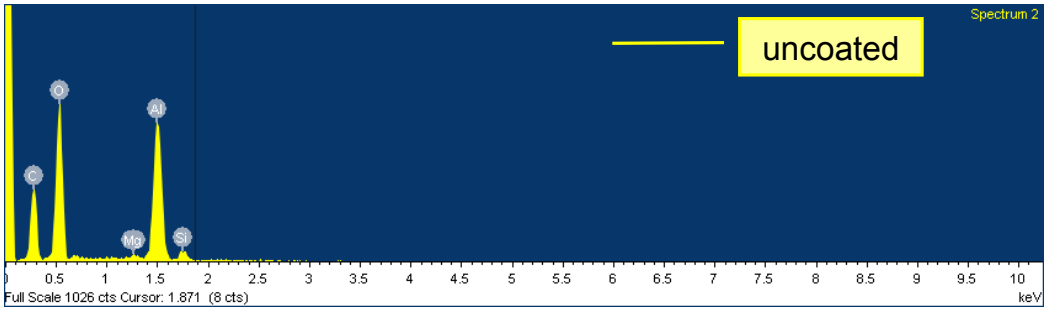


FIGURE 4. (A-D) PL spectra from Er, Sm, Nd, Cr

Scanning Electron Microscope and Energy dispersive X ray.
Scanning electrons microspcopy (SEM) and energy dispersive X ray (EDS) microanalysis were performed on coated test specimen. Figure 5 shown typical results of the as deposited coating in the test specimen. EDS analysis was employed to confirm and the presence of the optical centers on the coatings.







(B)

FIGURE 5. SEM and EDS spectrum of as deposited Er sol gel on a test specimen. (A) SEM-SE image (B) EDS spectra for the coated vs. uncoated region.

CONCLUSION

Significant work is underway toward the transition of smart polymeric coatings from solution and thin film material forms toward the identification of applications for containment verification and remote and unattended monitoring.

The investigation of smart coating can results in enhanced safeguards functionality and will improve present detection and tracking capabilities while ensuring continuation of knowledge and timeliness detection of possible diversion.

An extension of this work can result the in the development of concepts and approaches for multiple detection and structural health monitoring coatings that can be linked to e-pedigree technologies, radio frequency identification (RFID) and, 2-D barcodes, creating a true multilayered protective shield.

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