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Application of in-situ ion irradiation TEM and 4D tomography to advanced scintillator materials

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ABSTRACT

Scintillating nanomaterials are being investigated as replacements for fragile, difficult to synthesize single crystal radiation detectors, but greater insight into their structural stability when exposed to extreme environments is needed to determine long-term performance. An initial study using high-Z cadmium tungstate ($CdWO_4$) nanorods and an in-situ ion irradiation transmission electron microscope (I^3TEM) was performed to determine the feasibility of these extreme environment experiments. The I^3TEM presents a unique capability that permits the real time characterization of nanostructures exposed to various types of ion irradiation. In this work, we investigated the structural evolution of $CdWO_4$ nanorods exposed to 50 nA of 3 MeV copper (3+) ions. During the first several minutes of exposure, the nanorods underwent significant structural evolution. This appears to occur in two steps where the nanorods are first segmented into smaller sections followed by the sintering of adjacent particles into larger nanostructures. An additional study combined in-situ ion irradiation with electron tomography to record tilt series after each irradiation dose; which were then processed into 3D reconstructions to show radiation damage to the material over time. Analyses to understand the mechanisms and structure-property relationships involved are ongoing.

Keywords: TEM, in-situ ion irradiation, scintillator, cadmium tungstate, nanomaterials

1. INTRODUCTION

Radiation detection is critical for homeland security, nonproliferation, and national defense purposes. Many current research efforts focus on improving detector materials or developing novel ones to detect gamma rays up to 10 MeV and neutrons from fissile material, both of national security importance.[1] Inorganic detection materials are typically large single crystals of a semiconductor or scintillator compound, but these can be difficult to grow and process, leading to high cost and long production times.[2] Advanced scintillator materials require low costs and a possible decrease in the reliance on single crystals with improvement in energy resolution, specificity, detection efficiency, rapid decay times with no afterglow, radiation hardness, and mechanical ruggedness to allow high-throughput radiation screening on large scales.[1,3] Materials being investigated as novel inorganic scintillator materials to meet these needs include self-activated or Ce-activated compounds, polycrystalline ceramics, metal-organic frameworks, and nanoparticles all with the goal of competing with the current benchmarks NaI:Tl, CsI:Tl, and BGO.[1,4]

Cadmium tungstate ($CdWO_4$) has been used as a bulk single crystal scintillator for decades due to its high density, large light output, radiation hardness, ease of use (non-hygroscopic), high emission efficiency, low level of radioactive contamination, and low afterglow.[2,5,6] While this material works for some applications, there is desire to expand its use by eliminating the issues caused by single crystal processing. With the popularity of nanoscience rising in both chemistry and materials science, the scintillation properties of nanomaterials are becoming a pressing issue for applications from bioimaging to radiation detection. It is well known that the size and shape of nanomaterials are important determinants of the electronic and chemical behavior;[7] so it is a reasonable assumption that the ability to control the size and shape of nanomaterials made from known scintillators may lead to an ability to control the scintillation properties. This control could increase understanding of the structure-property relationships involved and permit property-specific materials engineering of novel radiation detection materials.[1]

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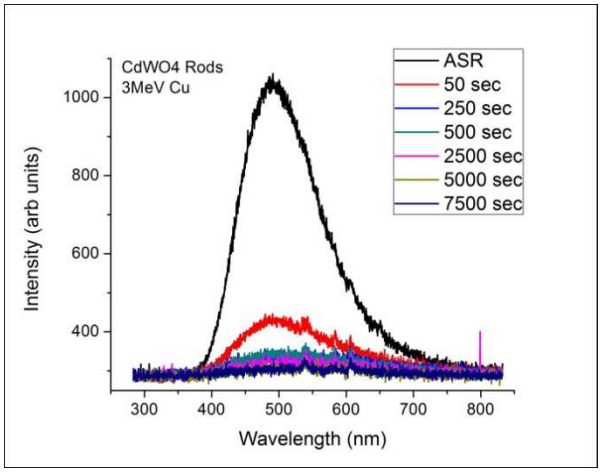

Figure 1: IBIL spectra of $CdWO_4$ nanorods irradiated with 50 nA of 3 MeV Cu^{3+}. Spectra show significant decrease in luminescence intensity with increased dose. ASR= as received.

We have synthesized $CdWO_4$ nanorods using a solution precipitation route and characterized the luminescence *via* ion beam induced luminescence which shows significant degradation with increased irradiation dose (Figure 1). In order to visualize this process, radiation hardness and radiation damage were studied using in-situ ion irradiation transmission electron microscopy (I^3TEM) and electron tomography. The I^3TEM is a unique capability that permits real time characterization of materials exposed to various types of particle bombardment. Imaging the internal microstructure during these events provides insight into the underlying mechanisms not gained through ex-situ irradiation and TEM characterization. In-situ ion irradiation has been used experimentally since the 1960s, but there are less than a dozen operational facilities at present.[8] Previous work on in-situ ion irradiation of nanomaterials has focused on particles embedded in a matrix,[9] but here the nanorods are simply placed on a TEM grid. Furthermore, we employed electron tomography to collect tilt series of the nanorods that are converted into 3D reconstructions to give a true-to-life view of the material rather than a 2D projection of a 3D object as in conventional TEM.[10] In tomography, images are recorded every 1-2° about a tilt axis and the collection of images is 'back-projected' to form the reconstruction.[7,10] The $CdWO_4$ nanorods were irradiated and images of various regions, or a tilt series of a single region, was recorded after each dose that when viewed together give a comprehensive view of the structural changes caused by increasing dose. A series of tomograms over time results in 4D tomography that shows radiation damage through the material, structural changes, and development of new structures such as sputtered particles. We show the utility of the I^3TEM and electron tomography in the study of radiation damage to scintillating nanomaterials, which can be used as part of a comprehensive characterization of the structure and properties of these materials.

2. EXPERIMENTAL

$CdWO_4$ nanorods used for these studies were synthesized *via* solution precipitation in which cadmium (II) acetate (0.34 g) and tungsten (VI) ethoxide (0.68 g) were added to a stirring solution of oleic acid (1.8 g) and trioctylamine (4.9 g). The solution was heated to reflux and held for 1 hr. Color changes were noted from orange to blue over the course of the reaction which reached a maximum temperature of 358°C. The heat was removed and the reaction was cooled to room temperature before extracting with chloroform. Nanorods were precipitated using ethanol and washed three times resulting in a light blue powder that easily redisperses in hexanes.[11] $CdWO_4$ nanorod TEM samples were prepared using 300 mesh, carbon type-B, copper grids from Ted Pella, Inc.

$CdWO_4$ nanorods were dispersed onto TEM grids and irradiated in-situ with 3 MeV Cu^{3+} ions. Two studies were conducted; one followed various regions with each irradiation exposure to track the change caused to different structures across the sample. The second was an electron tomography study of a single region in which a tilt series was recorded after each significant irradiation exposure and processed to yield a 3D reconstruction to aid visualization of the radiation damage to the sample.

All experiments were done using the in-situ ion irradiation TEM; a JEOL JEM-2100 operating at 200 kV with an ion beamline from a 6 MV Tandem Accelerator coming in at 90° to the electron beam (Figure 2). The ion beam was aligned through a series of beam burns done on plastic tape with a single tilt TEM holder. The stage was loaded and exposed to the ion beam for 30 sec and then removed. The ion beam was adjusted and subsequent beam burns completed until the burn area covered the grid area outlined on the holder tip. Sample irradiations are done at +31° tilt, the same tilt used for the beam burns and alignment. A sample grid was loaded into a double tilt stage with a -42° to +42° tilt range. For the initial study, 7 regions were imaged and then irradiated with 50 nA of 3 MeV Cu^{3+} for 15 min at a time. High energy, heavy ion irradiation using copper ions was chosen as an extreme case to determine the feasibility of these experiments and the capabilities of our system. This choice resulted in radiation doses that are much higher than these scintillator materials would experience in most practical environments. During each irradiation, one of the regions was tracked continuously on the TEM phosphor screen and was thus irradiated with both the electron and ion beams for the entire experiment. For some doses, video was recorded for the first five minutes or until sample drift resulted in the region of interest leaving the recording area and the phosphor screen was needed to reposition the sample. After each ion irradiation exposure, the sample was allowed to equilibrate and align before imaging; the process was repeated for a total irradiation time of 1 hr.

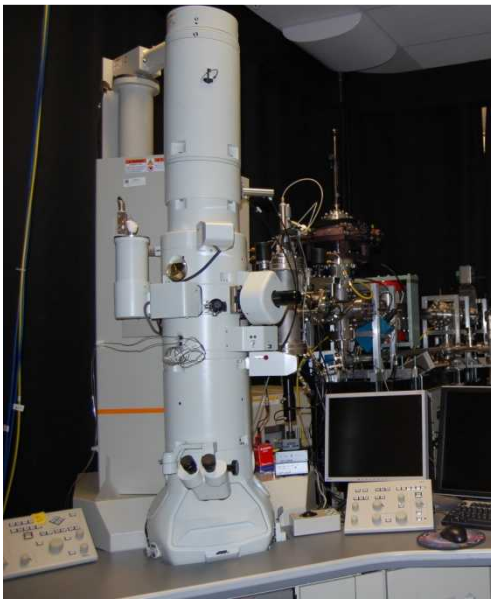

Figure 2: I^3TEM with beamline from 6 MV Tandem Accelerator coming into the TEM perpendicular to the column.

For tomography, the sample was loaded into the TEM as before. A region of interest was selected, and a tilt series, over the tilt range -42° to +42°, was recorded with images taken every 2°. The sample was irradiated with 30 nA of 3 MeV Cu^{3+} for 5 min and another tilt series was recorded. The final tilt series was recorded after a total irradiation time of 30 min. Each tilt series was processed into aligned tilt series videos using eTomo and 3dmod from the IMOD collection of processing and modeling programs available from the Boulder Laboratory for 3-D Electron Microscopy of Cells.[12,13] The 3D reconstructions of the region of interest were processed and recorded using the University of California, San Francisco Chimera package.[14] Viewing all three models side by side yields a 4D tomography analysis of the in-situ ion irradiation of $CdWO_4$ in which the radiation damage can be clearly seen as a function of increasing irradiation dose.

3. RESULTS AND DISCUSSION

To the best of our knowledge, this work represents the first in-situ ion irradiation experiments on nanotungstate scintillator materials. This is a vital step towards understanding the structure-property relationships in nanomaterials exposed to extreme radiation environments. We have verified the utility of the I^3TEM in providing the visualization that is crucial to understanding these relationships. The ability to record video during in-situ ion irradiation combined with still images and tomography for 3D reconstruction yields a comprehensive view of the material and the radiation damage

caused by irradiation. I^{3}TEM enables rapid analysis of a variety of materials and can employ a variety of ion beams at different energies that can be tuned for each experiment.

As prepared $CdWO_4$ nanorods appear fairly uniform in diameter, nominally 7 nm, and cluster together on the carbon-lace before irradiation. Figure 3 shows the irradiation induced changes to one of the tracked regions. After the first 15 min dose, the nanorods have fragmented into small, more spherical pieces. With subsequent doses, the small pieces recombine into larger structures while smaller nanoparticles (<2 nm diameter) appear on the carbon lace in regions where none were previously present. The small adjacent particles coalesce with one another into larger structures. We believe the nanorods break into pieces and coalesce, while simultaneous sputtering results in formation of smaller particles on nearby lace. More quantitative analysis is underway to elucidate the mechanisms at work and increase understanding of the processes observed as a function of irradiation dose.

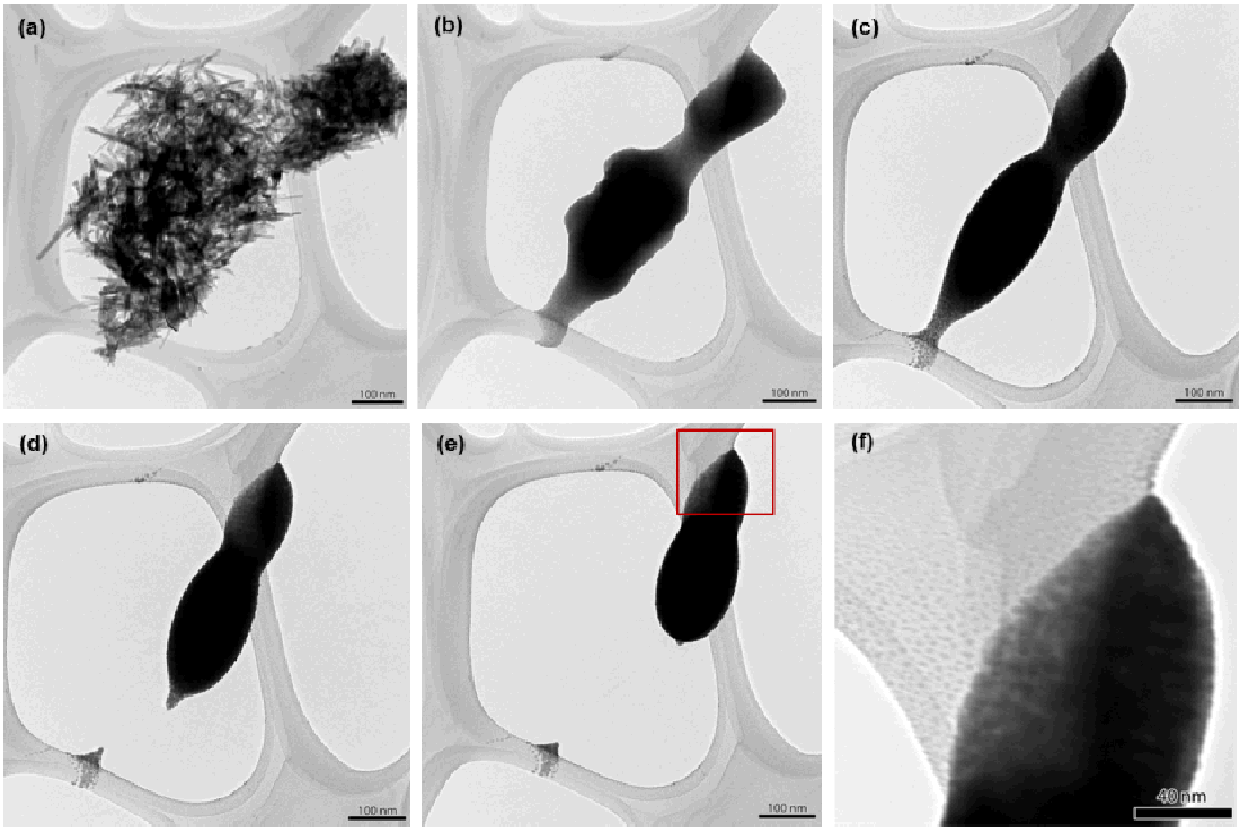

Figure 3: Region of $CdWO_4$ nanorods irradiated with 50 nA of 3 MeV Cu^{3+} (a) unirradiated, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, (f) magnification of red box in (e). Nanorods break into small pieces and small spherical particles sputter onto lace.

Electron tomography is becoming an important tool in both nanomaterial and irradiation research.[7,10] The ability to obtain 3D reconstructions of structures gives a better picture of the entire material and may aid in determining structure-property relationships. In this work, we combined in-situ ion irradiation with tomography by recording a tilt series on the $CdWO_4$ region of interest after each dose of irradiation. For each tilt series, the recorded images are compiled into an aligned tilt series that can be played as a continuous video. Since significant change was seen after 15 min in the initial studies (*vide supra*), the first irradiation dose for the tomography studies was only 5 min. The goal was to image some of the initial change, but to stop before the nanorods were unrecognizable. After 5 min, coalescence appears to have begun as rods are hard to distinguish in the middle of the cluster. The sample was irradiated for another 5 min, but little change was seen so irradiation continued until the total time was 30 min at which point, significant change had taken place. The rods appear coalesced, the edges are rounded, and the center appears denser with less rod structures sticking out. Individual rods can no longer be distinguished, as they all seem to have melted into one another and consolidated in the

center of the initial cluster. There is also noticeable accumulation of material on the edge of the carbon lace to the right of the region of interest; these are believed to be sputtered particles collecting on the lace as seen in the longer irradiation study. The three tomography reconstructions are shown in Figure 4, making the change over time and increased radiation dose readily apparent. This 4D tomography clearly shows the extent of the radiation damage and sputtering of the material. As the mechanisms are better understood, these reconstructions will help us figure out how, and perhaps why, properties, such as total scintillation intensity and relative peak intensity, change as the structure changes.

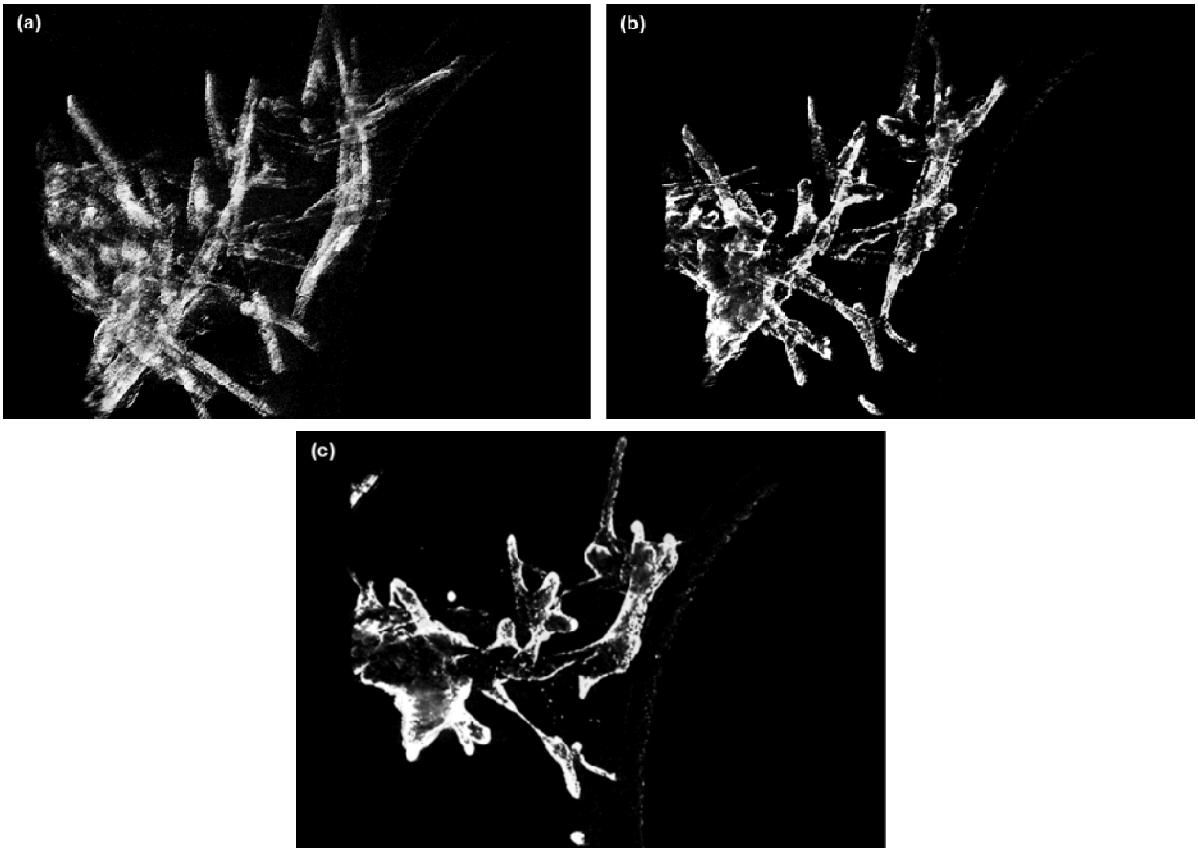

Figure 4: 3D reconstructions of tomography tilt series of $CdWO_4$ nanorods irradiated with 30 nA of 3 MeV Cu^{3+} (a) unirradiated, (b) 5 min, (c) 30 min. Models show the coalescence of the rods and the collection of smaller particleson edge of lace.

While significant damage in the form of coalescence and sputtering was observed, the majority of the material did stay on the lace and the changes could be tracked. This proves studying nano-scintillator materials using the I^3TEM is feasible, and it is expected less damage will be seen with lower radiation doses. Recently, we have begun irradiating the $CdWO_4$ nanorods with 100 nA of 2.5 MeV protons (H^+) as a first order simulation of neutrons. Little to no change has been seen after irradiation studies of up to 4 hr. Studies will also be done using only electron irradiation to simulate gamma rays, which bulk $CdWO_4$ is currently used to detect.[2,5,6] Preliminary results suggest that the radiation hardness observed in bulk $CdWO_4$ crystals[5] appears to be retained at the nanoscale, but more work is needed to quantify this initial assessment.

Currenlty, an optical pathway is being developed and added to the I^3TEM that should permit in-situ cathodoluminescence (CL) and ion beam induced luminescence (IBIL) studies. This will be accomplished by inserting an angled mirror with a bore hole for the electron path on top of the objective polepiece in the heart of the TEM. These additions will not inhibit the function of the TEM or in-situ ion irradiation, but will enhance the system's capabilities. If successful, the combined abilities will enable in-situ structure-property relationship studies as the luminescence of a material can be tested during ion irradiation. CL and IBIL will be performed on the same areas imaged and irradiated in

the TEM leading to direct correlation between images or tomography tilt series and luminescence data as all sample, environment, and beam conditions will be identical.

4. CONCLUSION

We have shown I^3TEM to be useful for studying the structural evolution of $CdWO_4$ nanorod scintillator materials caused by an extreme radiation environment. $CdWO_4$ was irradiated with 50 nA of 3 MeV Cu^{3+} and images were recorded of 7 regions every 15 min. The rods broke into small pieces that then recombined into larger structures and smaller particles sputtered off onto the nearby carbon lace of the TEM grid. In a later study, $CdWO_4$ nanorods were irradiated with 30 nA of 3 MeV Cu^{3+} and tilt series over an 84° degree range were recorded on the unirradiated material, after 5 min, and after 30 min. The tilt series were processed to yield 3D reconstructions that show radiation damage to the material. Again, the nanorods appear to coalesce and sputter. Viewing all three tomographic models together gives a 4D visualization of the structural changes caused by increased time and dose that may be useful in determining structure-property relationships. Work towards understanding the mechanisms and processes leading to the structural changes and radiation damage observed is ongoing.

Studies have begun using H^+ irradiation to simulate neutrons, effective detection of which is a pressing need in the scintillator and radiation detection community.[1] To date, the nanorods appear to undergo little to no change with continued H^+ irradiation. Additional studies to confirm results and perform tomography will be conducted. Furthermore, planned additions to the I^3TEM, if successful, will permit in-situ CL and IBIL measurements that would enable thorough structure-property relationship studies. These comprehensive experiments will allow direct correlation between images or tomographic models and luminescence analyses. The ongoing and future work will take advantage of many of the unique capabilities of the I^3TEM and lead to novel studies of nano-scintillator materials that should greatly increase understanding of scintillation behavior as a function of radiation dose, paving the way for enhanced nanomaterial engineering.

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