The use of tungstate nanoparticles in hybrid X-ray detectors

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ABSTRACT Hybrid materials composed of an organic matrix with high-Z nanoparticles have a high potential to be used for radiation detection purposes. In this study, scheelite and wolframite tungstates with different crystallinity were prepared using co-precipitation and hydrothermal synthesis. Nano- and polycrystalline powders were characterized by X-ray diffraction, scanning electron microscopy, X-ray absorption spectroscopy, Raman spectroscopy and X-ray excited optical luminescence. Novel hybrid organic-inorganic systems were fabricated based on a mixture of tungstate nanoparticles with P3HT:PCBM blend, and their performance was tested using synchrotron radiation in a wide energy range.

INTRODUCTION

The development of new radiation detectors based on nanomaterials is currently an active area of research [1,2]. Here, we propose a new class of materials, namely tungstates with a general formula AWO_4 (where A is a divalent ion), for use in hybrid organic-inorganic systems for X-ray detection.

Tungstates of divalent metals form a large class of materials with various applications including but not limited to scintillators, photocatalysis, supercapacitors and sensors. The high-Z value of tungsten (Z=74) and the possibility to vary the atomic number of the second cation in a wide range (Z=12 for Mg, Z=56 for Ba) make tungstates attractive for the development of novel hybrid organic-inorganic X-ray detectors.

In this study, hybrid organic-inorganic systems were fabricated based on a mixture of tungstate nanoparticles (NPs) with P3HT:PCBM blend. NPs prepared using co-precipitation (CoP) and hydrothermal (HDT) synthesis were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray absorption spectroscopy (XAS), Raman spectroscopy and X-ray excited optical luminescence (XEOL). Obtained hybrid systems were used to fabricate X-ray detectors operating without bias voltage, and their performance was tested using synchrotron radiation in a wide energy range.

Table 1. Absorption edges of selected elements [4].

Element	Edge	Energy
Ca	K	4038.5 eV
Zn	K	9659 eV
W	L_3	10207 eV
Sr	K	16105 eV
Cd	K	26711 eV

Fig. 1. Structures of scheelite-type tungstate composed of WO_4 tetrahedra and eight-fold coordinated A^{2+} ions (a); wolframite-type tungstate built up of distorted WO_6 and AO_6 octahedra (b); P3HT (Poly(3-hexylthiophene-2,5-diyl)) (c) and PCBM (Phenyl-C61-butyric acid methylester) (d).

X-ray detectors

Hybrid organic-inorganic X-ray detectors were fabricated on top of the 25×25 mm ITO-coated glass. PEDOT:PSS layer was spin coated in air and annealed at 150°C for 10 min. Thin films from P3HT:PCBM and NPs suspension were made by blade-casting on a substrate heated to 75 °C. BPhen (5 nm) and Al electrodes (100 nm) were deposited by thermal evaporation in vacuum.

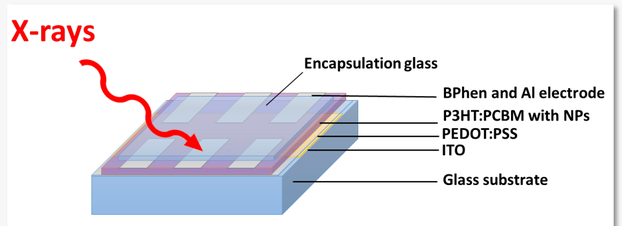

Fig. 7. A schematic representation of fabricated hybrid organic-inorganic X-ray detectors.

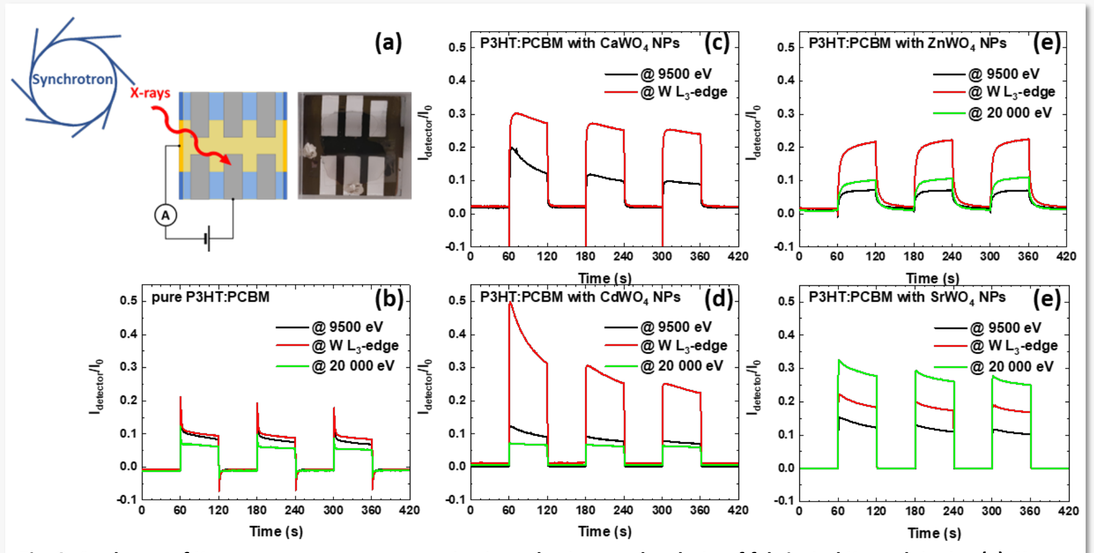

Fig. 8. A scheme of X-ray response measurements at synchrotron and a photo of fabricated X-ray detector (a). X-ray response signal ($I_{detector}/I_0$) for pure P3HT:PCBM (b) and hybrid (c-f) detectors during irradiation On-Off cycles. All detectors respond to irradiation with X-rays without bias voltage.

X-ray diffraction (XRD)

Scheelite (A=Ca, Sr) and wolframite-type (A=Zn, Cd) tungstates with different crystallinity were prepared using co-precipitation (CoP) at room temperature (RT) and hydrothermal (HDT) synthesis at 160°C. CoP at RT results in agglomerated NPs with an average crystallite size *d* of 10-30 nm but using citric acid (CA) as a capping agent the average size of NPs was smaller than 5-6 nm.

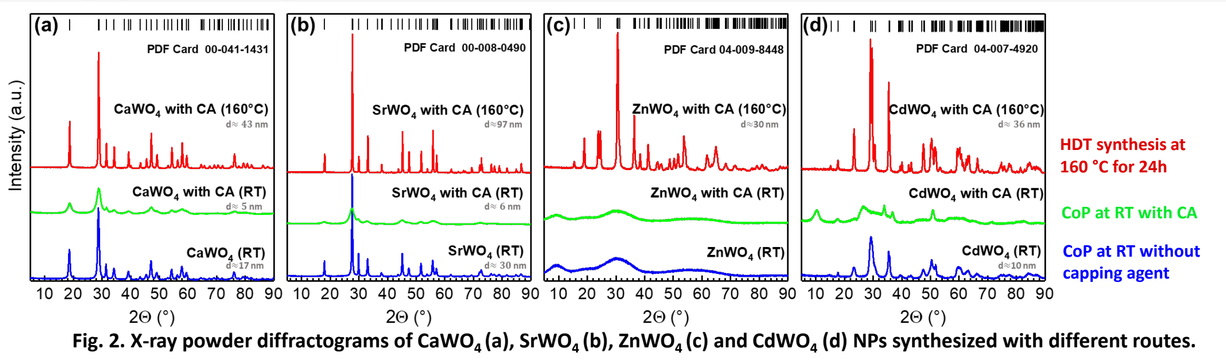

Fig. 2. X-ray powder diffractograms of $CaWO_4$ (a), $SrWO_4$ (b), $ZnWO_4$ (c) and $CdWO_4$ (d) NPs synthesized with different routes.

CONCLUSIONS

- Different synthesis parameters affect the size and morphology of NPs. Citric acid works as a capping agent and limits growth of NPs.
- In EXAFS spectra, size-induced local structure relaxations are observed which are more pronounced in NPs of wolframite-type.
- XEOL is suppressed in NPs with low crystallinity because of high lattice defect concentration.
- Hybrid X-ray detectors were composed of hydrothermally synthesized tungstate NPs and P3HT:PCBM blend. The presence of NPs with high-Z elements improves the response to X-rays compared to pure P3HT:PCBM.
- These results suggest that nanocrystalline tungstates are good candidates for use in hybrid organic-inorganic X-ray detectors.

X-ray absorption spectroscopy

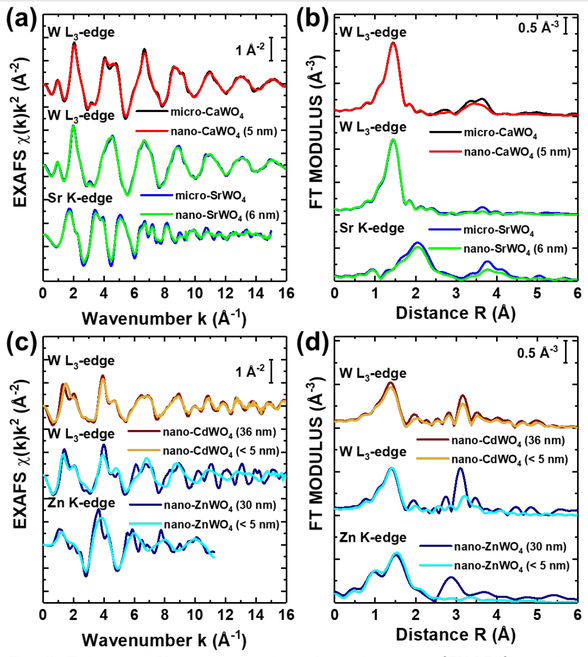

Fig. 3. Extended X-ray absorption fine structure (EXAFS) spectra (a,c) and corresponding Fourier transforms (FTs) of different crystallinity tungstate samples at the W L_3-edge and Sr, Zn K-edges. Size-induced local structure relaxations are observed.

Raman spectroscopy

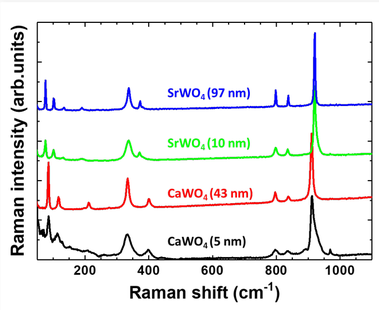

Fig. 4. Raman spectra of different crystallinity scheelite-type $CaWO_4$ and $SrWO_4$ samples. Size-induced Raman peak broadening is observed.

X-ray induced optical luminescence

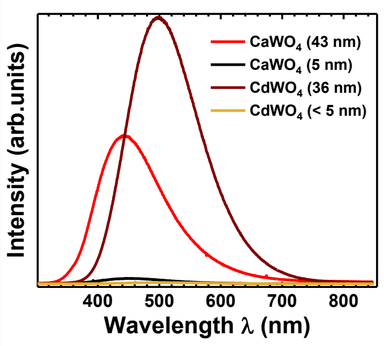

Fig. 5. X-ray induced optical luminescence spectra of different crystallinity scheelite-type $CaWO_4$ and wolframite-type $CdWO_4$ samples. For different types of tungstates, the luminescence maximum is at different wavelengths. XEOL is suppressed in NPs with low crystallinity.

Scanning electron microscopy

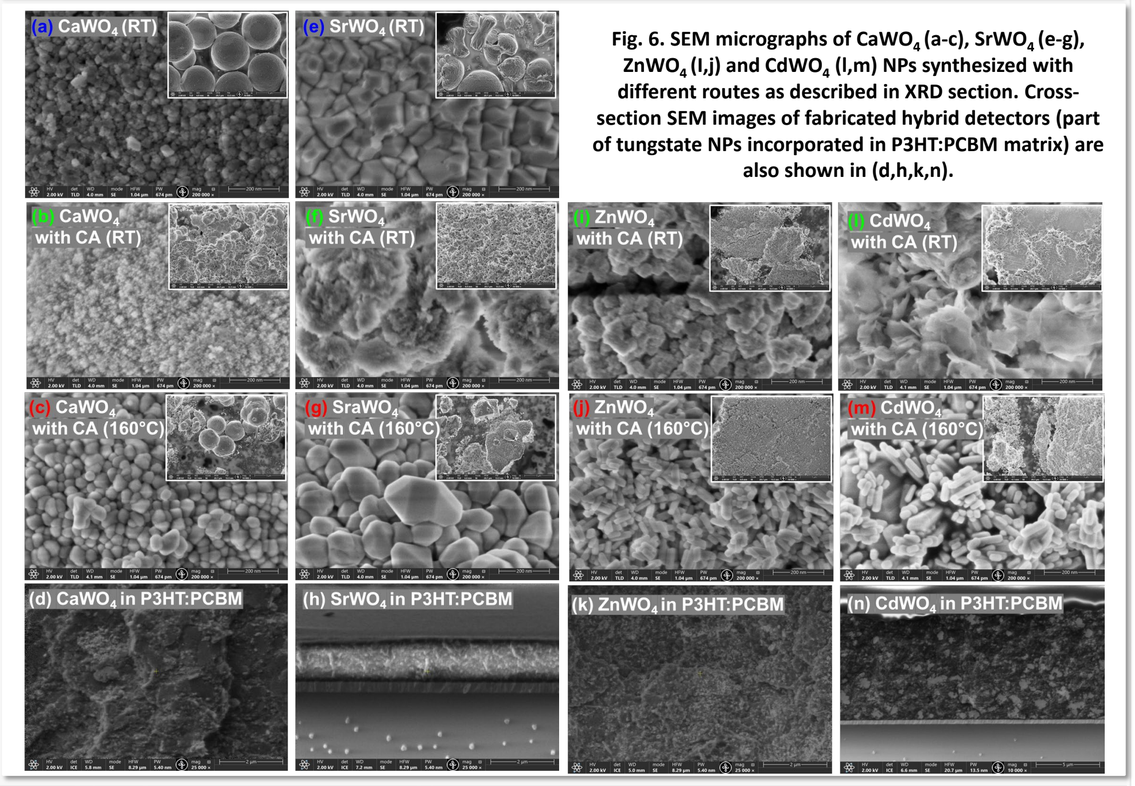

Fig. 6. SEM micrographs of $CaWO_4$ (a-c), $SrWO_4$ (e-g), $ZnWO_4$ (I,j) and $CdWO_4$ (l,m) NPs synthesized with different routes as described in XRD section. Cross-section SEM images of fabricated hybrid detectors (part of tungstate NPs incorporated in P3HT:PCBM matrix) are also shown in (d,h,k,n).

References

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