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Formation mechanism and optical/magnetic properties of high-entropy (FeCuMn)(WMo)O_{4-x}S_x nanosheets synthesized via hydrothermal method

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Abstract: Breaking the NIR-II bottleneck, conventional inorganic semiconductors have long suffered from inadequate optical absorption, limiting their phototherapeutic efficacy. Here, we report a paradigm-shifting breakthrough: the first-ever hydrothermal synthesis of high-entropy (FeCuMn)(WMo)O_{4-x}S_x nanosheets. By overcoming the fundamental immiscibility of five transition metals, our monoclinic nanosheets unlock an unprecedented broadband absorption spanning 400–1400 nm, achieving record-high photothermal conversion in both the NIR-I and NIR-II biological windows ($\Delta T = 38\text{ }^{\circ}\text{C}$ at 808 nm). Remarkably, this high-entropy configuration simultaneously endows the material with strong T_1/T_2 magnetic relaxivity, enabling novel dual-modal MR imaging capability. This first demonstration of integrating photothermal and magnetic functionalities via hydrothermal high-entropy engineering opens a new avenue for theranostic nanoplatforms.

Keywords: High-entropy materials; Hydrothermal synthesis; Photothermal therapy; Magnetic resonance imaging; Nanosheets

1. Introduction

Nanomaterials possessing both optical and magnetic properties have emerged as promising platforms for cancer theranostics, enabling non-invasive treatment and real-time diagnosis through their enhanced permeability and retention (EPR) effect in tumor tissues [1,2]. The integration of multiple therapeutic modalities on a single nanoplatform, rather than simple mixing of individual agents, is crucial for achieving synergistic therapeutic efficacy. High-entropy materials (HEMs), characterized by their unique configurational entropy stabilization and multi-element composition, offer a compelling strategy to integrate diverse functionalities including photothermal conversion, catalytic activity, and magnetic resonance imaging (MRI) contrast enhancement [3,4].

Near-infrared (NIR) laser-responsive nanomaterials have attracted considerable attention for photothermal therapy (PTT) and photodynamic therapy (PDT) due to their minimal invasiveness, precise spatial selectivity, and rapid recovery compared to conventional cancer treatments [5,6]. The NIR-I biological window (750–1000 nm) has been extensively explored, yet the NIR-II window

(1000–1350 nm) offers superior therapeutic performance due to reduced tissue scattering and absorption, deeper penetration depth, and higher maximum permissible exposure [7]. However, conventional inorganic semiconductors such as MoS₂, WS₂, and FeS₂ exhibit strong absorption in the NIR-I region but limited optical properties in the NIR-II biowindow [8,9]. Recently, high-entropy oxides have demonstrated enhanced NIR absorption and photothermal conversion properties in the NIR biological window, attributed to their compositional diversity and lattice distortion effects [10].

High-entropy ceramics (HECs), typically containing five or more metal elements in single-phase systems, exhibit unique physicochemical properties derived from the high-entropy effect, lattice distortion, and sluggish diffusion [11,12]. These materials have shown exceptional thermal stability, mechanical properties, and tunable electrical and magnetic characteristics, making them attractive for biomedical applications [13,14]. The incorporation of multiple elements enables the simultaneous optimization of optical absorption, magnetic relaxation, and catalytic activity, overcoming the limitations of conventional single-component inorganic nanomaterials.

In this work, we report the first hydrothermal synthesis of high-entropy (FeCuMn)(WMo)O_{4-x}S_x nanosheets (HEFWOS) with a monoclinic structure. The strategic selection of constituent elements is based on their complementary functionalities: Fe and Mn serve as MR imaging agents (T₂ and T₁ contrast, respectively), while W provides CT imaging capability. The incorporation of sulfur via thiourea hydrolysis enables bandgap engineering to extend optical absorption into the NIR-II region. The high-entropy configuration is expected to enhance photothermal conversion efficiency through lattice distortion-induced band structure modification and multiple electronic transition pathways. Our systematic investigation of the formation mechanism via XRD, XPS, and TEM reveals the critical role of temperature in overcoming immiscibility limits and achieving compositional homogeneity. The resulting nanosheets exhibit broadband absorption spanning 400–1400 nm, high photothermal conversion efficiency in both NIR-I and NIR-II windows, and strong T₁/T₂ magnetic relaxivity, positioning HEFWOS as a promising theranostic platform for MRI-guided phototherapy.

2. Experimental section

2.1 Materials

Copper(II) chloride dihydrate (CuCl₂·2H₂O, ≥99.9%), iron(II) chloride tetrahydrate

($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\geq 99.0\%$), sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99.5\%$), sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99.5\%$), and manganese(II) chloride anhydrous (MnCl_2 , $\geq 98.0\%$) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Thiourea ($\text{CH}_4\text{N}_2\text{S}$, $\geq 99.0\%$), ethylene glycol (EG, $\geq 99.5\%$), polyvinylpyrrolidone (PVP, $M_w \approx 40,000$), sodium hydroxide (NaOH , $\geq 98.0\%$), and hydrochloric acid (HCl , 37%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Thiol-terminated polyethylene glycol (SH-PEG, $M_w \approx 5,000$) was obtained from Shanghai Yare Biotech Co., Ltd. (Shanghai, China). All chemicals were of analytical reagent grade and used as received without further purification. Deionized (DI) water with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$ was used throughout all experiments.

2.2 Synthesis of HEFWOS nanosheets

High-entropy $(\text{FeCuMn})(\text{WMo})\text{O}_{4-x}\text{S}_x$ (HEFWOS) nanosheets were synthesized via a modified one-pot hydrothermal method. In a typical procedure, 0.2 mmol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.2 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 0.2 mmol MnCl_2 , 0.2 mmol $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, and 0.2 mmol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 10 mL of DI water containing 0.2 mL of HCl (1%, v/v), 0.5 g of PVP, and 4 mL of EG under magnetic stirring for 30 min to form a homogeneous transparent solution. Subsequently, 1 mL of NaOH aqueous solution (1 M) was added dropwise under continuous stirring for 60 min, during which the solution color changed from green to brown, indicating the formation of metal hydroxide/oxide precursors. Then, 2 mmol of thiourea was introduced into the suspension and stirred for an additional 60 min to ensure complete dissolution.

The resulting mixture was transferred into a 20 mL Teflon-lined stainless-steel autoclave, sealed, and heated at different temperatures (140, 160, 180, and 200 °C) for 4 h in an electric oven. To investigate the effect of reaction time, additional experiments were conducted at 200 °C for 6, 12, and 24 h. After hydrothermal treatment, the autoclave was allowed to cool naturally to room temperature. The obtained precipitates were collected by centrifugation at 10,000 rpm for 10 min, washed thoroughly with DI water and absolute ethanol alternately for at least three cycles, and finally dried at 60 °C for 12 h in a vacuum oven for further characterization.

2.3 Surface PEGylation of HEFWOS

To enhance colloidal stability and biocompatibility, HEFWOS nanosheets were modified with thiol-terminated polyethylene glycol (SH-PEG). Briefly, 20 mg of as-prepared HEFWOS powder was dispersed in 10 mL of DI water containing 50 mg of SH-PEG ($M_w \approx 5,000$) under vigorous

magnetic stirring at room temperature for 12 h. The PEGylated HEFWOS (HEFWOS-PEG) were collected by repeated centrifugation at 15,000 rpm for 10 min, washed with DI water three times to remove excess free PEG, and finally re-dispersed in DI water and stored at 4 °C for subsequent characterization and photothermal experiments.

2.4 Characterization

The crystalline structure and phase composition of the synthesized samples were determined by powder X-ray diffraction (XRD) using a PANalytical X'pert PRO diffractometer (Netherlands) with Cu K α radiation ($\lambda = 0.15406$ nm) operating at 40 kV and 40 mA, with a scanning rate of $5^\circ \cdot \text{min}^{-1}$ over the 2θ range of 10° – 80° . The surface chemical composition and elemental valence states were analyzed by X-ray photoelectron spectroscopy (XPS) on an ESCALab 250Xi spectrometer (Thermo Fisher Scientific, USA) using monochromatized Al K α X-ray source ($h\nu = 1486.6$ eV). All binding energies were calibrated with reference to the C 1s peak at 284.8 eV.

The morphology, size, and microstructure were observed using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) on a JEOL JEM 3010 microscope (Japan) operating at an accelerating voltage of 300 kV. Selected area electron diffraction (SAED) patterns were acquired to confirm the crystal structure. High-angle annular dark-field scanning TEM (HAADF-STEM) images and corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping were performed on an FEI Talos F2000X S/TEM (USA) equipped with a Super-X EDS detector at 200 kV to evaluate the elemental distribution and compositional homogeneity.

The UV-Vis-NIR absorption spectra of HEFWOS aqueous dispersions were recorded on a PerkinElmer Lambda 750 spectrophotometer (USA) using a 1 cm quartz cuvette in the wavelength range of 300–1500 nm. The magnetic properties were measured using a vibrating sample magnetometer (VSM, VSM 7400, USA) at room temperature in an applied magnetic field range of ± 20 kOe.

2.5 Photothermal performance evaluation

To evaluate the photothermal conversion capability, HEFWOS-PEG aqueous dispersions at different concentrations (0, 50, 100, and 200 $\mu\text{g} \cdot \text{mL}^{-1}$) were prepared in 1.5 mL quartz cuvettes. Each dispersion (1 mL) was irradiated with continuous-wave diode lasers at wavelengths of 808 nm, 976 nm, and 1064 nm, respectively, with a fixed power density of $1.5 \text{ W} \cdot \text{cm}^{-2}$ for 5 min. The laser beam spot diameter was adjusted to 6 mm to ensure uniform illumination. The temperature of the

dispersions was monitored in real-time using an infrared thermal camera (Fortric 225, China) and recorded at 10 s intervals. The ambient temperature was maintained at 25 ± 0.5 °C throughout the measurements.

3. Results and discussion

3.1 Synthesis and formation mechanism of HEFWOS nanosheets

The synthesis of high-entropy (FeCuMn)(WMo)O_{4-x}S_x (HEFWOS) nanosheets involves a complex reaction system due to the coexistence of multiple metal cations (Mn²⁺, Fe²⁺, Cu²⁺, Mo⁶⁺, W⁶⁺) and anions (OH⁻, O²⁻, S²⁻). The solution chemistry during precursor preparation plays a critical role in determining the final product composition and homogeneity.

Under acidic conditions (pH $\approx$ 2–3, adjusted by 1% HCl), all metal salts were fully dissolved in the aqueous solution containing EG and PVP, resulting in a transparent green solution (Fig. 1a). The green color primarily originated from Cu²⁺ and Fe²⁺ ions. Upon the dropwise addition of NaOH solution, the pH gradually increased to approximately 7.5, triggering the simultaneous precipitation of metal hydroxides and oxides. The solution color rapidly changed from green to brown (Fig. 1b), indicative of the formation of amorphous or poorly crystalline hydroxide/oxide precursors, including Cu(OH)₂, Fe(OH)₂, Mn(OH)₂, H₂MoO₄, and H₂WO₄. Under alkaline conditions, the divalent metal cations (Mn²⁺, Fe²⁺, Cu²⁺) readily formed hydroxide precipitates, while molybdate (MoO₄²⁻) and tungstate (WO₄²⁻) ions may have co-precipitated with these hydroxides or formed insoluble metal molybdates/tungstates via metathesis reactions. The as-obtained precursor slurry exhibited poor crystallinity, as confirmed by XRD analysis (Fig. 1c), which showed only broad and weak diffraction peaks without well-defined reflections, indicating the amorphous nature of the precipitates.

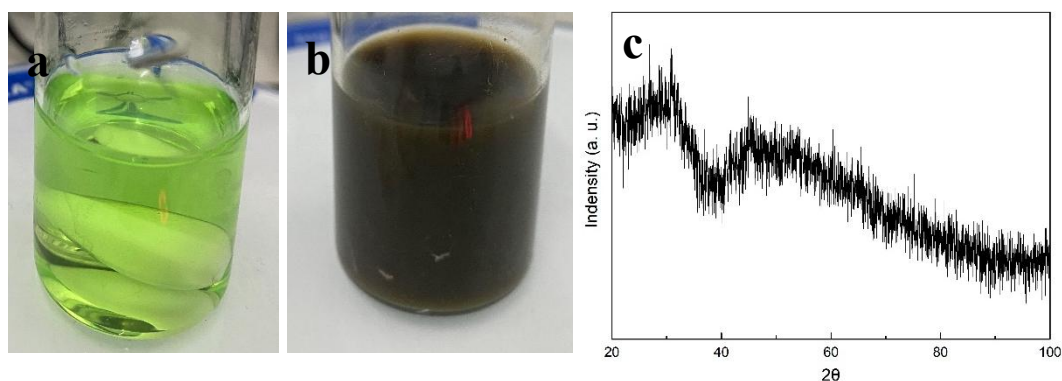


Fig. 1 (a) Liquid under acidic condition, (b) Liquid under alkaline condition, (c) XRD of suspension

The hydrothermal synthesis temperature plays a decisive role in determining the phase composition and purity of the final products. As shown in Fig. 2, Fig. 3, Fig. 4, and Fig. 5, the products obtained at different temperatures exhibited distinctly different phase constitutions. When the hydrothermal reaction was conducted at 140 °C for 4 h, a biphasic mixture was obtained, consisting of a CuFeS₂ impurity phase alongside the target high-entropy (FeCuMn)(WMo)O_{4-x}S_x (HEFWOS) phase, as identified by XRD analysis (Fig. 2a). In contrast, when the synthesis temperature was elevated to 200 °C under otherwise identical conditions, a single-phase HEFWOS solid solution was successfully achieved, with no detectable impurity peaks, indicating complete dissolution of all constituent elements into a homogeneous monoclinic structure.

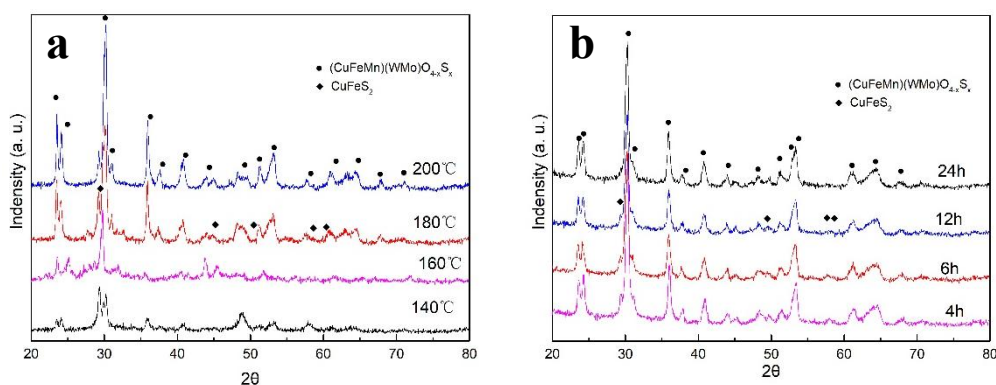


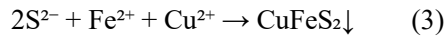
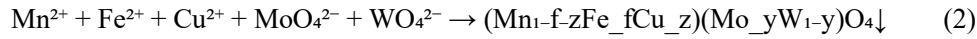
Fig. 2 XRD patterns of samples: (a) synthesized at different temperature for 4 h, (b) synthesized at 200 °C for different time

Based on the comprehensive experimental observations, the overall reaction pathway during hydrothermal treatment can be rationally described by the scheme illustrated in Fig. 3. The formation of both the intermediate CuFeS₂ phase and the final HEFWOS solid solution is closely associated with the in-situ hydrolysis of thiourea, which serves as a slow-release sulfur source. The hydrolysis of thiourea under hydrothermal conditions proceeds according to the following equation [19]:

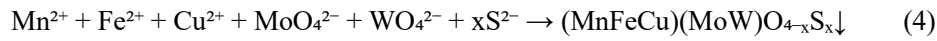
$$(\text{NH}_2)_2\text{CS} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2\uparrow + 2\text{NH}_3\uparrow + \text{H}_2\text{S}\uparrow \quad (1)$$

The gradually released H₂S dissociates to provide S²⁻ ions, which participate in the competitive precipitation and crystallization reactions with metal cations. At lower temperatures (140 °C), the formation kinetics favor the selective precipitation of CuFeS₂, a stable binary sulfide phase, likely due to the strong covalent bonding affinity between Cu⁺/Fe²⁺ and S²⁻ under sulfur-rich local environments. Concurrently, the remaining metal species (primarily Mn²⁺, Mo⁶⁺, and W⁶⁺) precipitate as metal oxides or oxysalts, forming a multiphase mixture rather than a homogeneous

solid solution. This competitive reaction can be represented by the following simplified equations:



At elevated temperatures ($\geq 180\text{--}200\text{ }^\circ\text{C}$), the increased thermal energy promotes enhanced ionic diffusion kinetics and overcomes the kinetic barriers for the mutual dissolution of multiple metal species. The high configurational entropy ($\Delta S_{\text{conf}} = R \ln N$, where $N \geq 5$ for the five metal elements) becomes thermodynamically favorable, driving the system toward a single-phase solid solution. Under these conditions, the sulfur anions partially substitute oxygen anions in the tungstate/molybdate lattice, leading to the formation of the oxysulfide solid solution, which can be expressed as:



where x represents the degree of sulfur substitution, which is governed by the thiourea concentration and hydrothermal temperature.

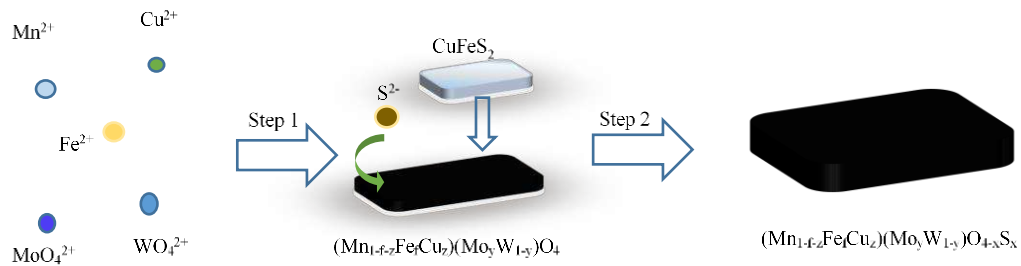


Fig. 3 Formation mechanism of HEFMOS

To systematically investigate the formation mechanism, a series of controlled syntheses were conducted at varying hydrothermal temperatures (140, 160, 180, and $200\text{ }^\circ\text{C}$) and reaction times (4, 6, 12, and 24 h). As shown in Fig. 2(a), the product synthesized at $140\text{ }^\circ\text{C}$ for 4 h consisted of a mixture of poorly crystalline HEFWOS and CuFeS_2 phases. With increasing temperature, a systematic evolution in phase composition was observed: the diffraction peaks gradually intensified and shifted toward higher 2θ angles, indicating improved crystallinity and progressive lattice contraction, while the CuFeS_2 -related peaks diminished and eventually disappeared at temperatures above $180\text{ }^\circ\text{C}$. Concurrently, the crystal structure of the HEFWOS phase gradually transitioned from

a MnWO_4 -type configuration toward a FeWO_4 -type configuration, both sharing the same P2/c (No. 13) space group symmetry.

XRD analysis of the product synthesized at 140 °C (Fig. 3a) revealed eight distinct diffraction peaks located at $2\theta = 23.5^\circ, 24.1^\circ, 29.8^\circ, 30.3^\circ, 31.1^\circ, 37.0^\circ, 53.3^\circ$, and 61.5° , which are in good agreement with the standard diffraction pattern of monoclinic MnWO_4 (JCPDS No. 13-0345). Additional diffraction peaks at $29.4^\circ, 48.3^\circ, 49.0^\circ, 57.8^\circ$, and 58.5° can be indexed to the (112), (220), (204), (312), and (116) planes of tetragonal CuFeS_2 (JCPDS No. 37-0471).

The reaction time exerts a similar but less pronounced influence on the phase evolution, as depicted in Fig. 2(b). At a fixed temperature of 200 °C, extending the reaction time from 4 h to 24 h resulted in progressive enhancement of diffraction peak intensity, increased crystallinity, and further peak shifts toward higher angles, indicating continued lattice relaxation and compositional homogenization. However, unlike temperature, prolonged reaction time alone could not eliminate the CuFeS_2 impurity at temperatures below 160 °C.

The lattice distortion induced by the incorporation of multiple metal cations is responsible for the observed peak shifts. Shannon ionic radii for octahedral/tetrahedral coordination are: $\text{Mn}^{2+} = 0.83 \text{ \AA}$, $\text{Fe}^{2+} = 0.78 \text{ \AA}$, $\text{Cu}^{2+} = 0.73 \text{ \AA}$, $\text{Mo}^{6+} = 0.59 \text{ \AA}$, $\text{W}^{6+} = 0.60 \text{ \AA}$, $\text{O}^{2-} = 1.40 \text{ \AA}$, and $\text{S}^{2-} = 1.84 \text{ \AA}$. The size mismatch introduces local strain fields and modifies the interplanar spacings, resulting in the systematic shift of diffraction peaks.

To further elucidate the phase distribution and elemental segregation, TEM observations and STEM-EDS elemental mapping were conducted. As shown in Fig. 4, the HAADF-STEM image and corresponding EDS maps reveal a heterogeneous elemental distribution for the 140 °C-synthesized sample, with W, Mn, and O enriched in certain regions and Cu, Fe, and S concentrated in segregated domains, consistent with the coexistence of MnWO_4 -type and CuFeS_2 phases. In stark contrast, the sample synthesized at 200 °C for 24 h (Fig. 5) displays a remarkably uniform distribution of all constituent elements—Mn, Fe, Cu, Mo, W, O, and S—throughout the entire nanosheet.

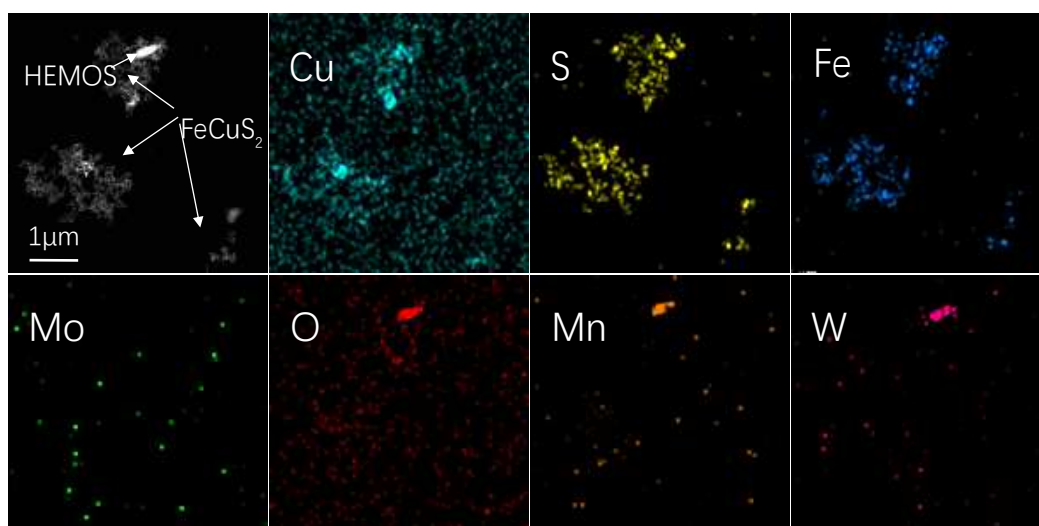


Fig. 4 HAADF-STEM image and EDS elemental maps of sample synthesized at 140 °C

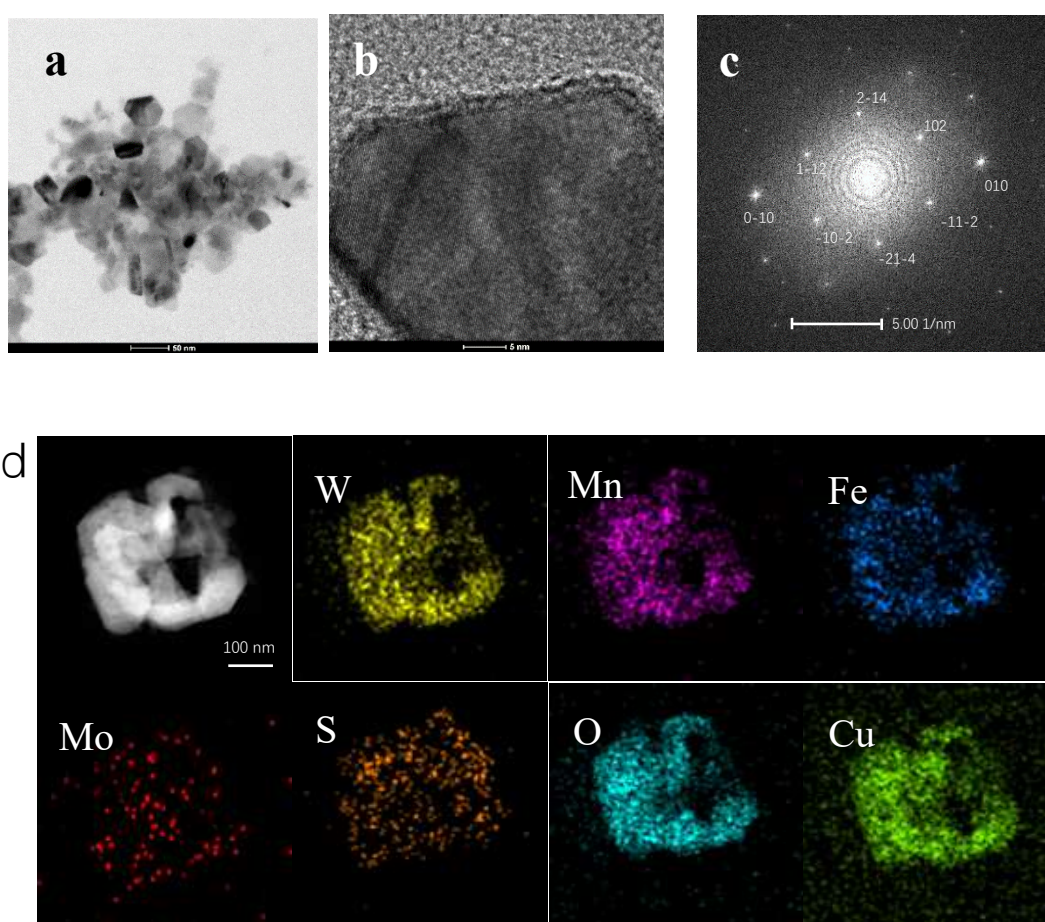


Fig. 5 sample synthesized at 200 °C for 24 h: (a) Low-magnification TEM image, (b) HRTEM image, (c) the corresponding SAED pattern, (d) HAADF-STEM image and EDS elemental maps

The low-magnification TEM images (Fig. 4 and Fig. 5a) reveal that the prepared particles exhibit a sheet-like morphology (nanosheets) with lateral dimensions generally below 100 nm. The SAED pattern of the 200 °C-synthesized sample (Fig. 5b) exhibits well-defined diffraction spots

indexed to the (010), (102), ($\overline{1}12$), and (214) planes of the monoclinic P2/c structure. HRTEM imaging (Fig. 5c) reveals lattice fringes with an interplanar spacing of 0.258 nm, corresponding to the (030) plane, slightly smaller than the reported d-spacing for pure FeWO₄ (0.262 nm, JCPDS No. 13-0345), confirming lattice contraction due to solid solution formation.

3.2 Chemical state analysis by XPS

To elucidate the chemical states and bonding configurations of the constituent elements, XPS analysis was performed (Fig. 6). The survey spectrum confirms the presence of Mn, Fe, Cu, Mo, W, O, and S. The S 2p spectrum exhibits a doublet at 161.5 eV (S 2p_{3/2}) and 162.7 eV (S 2p_{1/2}), characteristic of S²⁻ (formal valence -2), with no sulfate peaks (>168 eV) detected. The O 1s spectrum can be deconvoluted into lattice oxygen (529.8 eV) and surface-adsorbed hydroxyl species (531.5 eV).

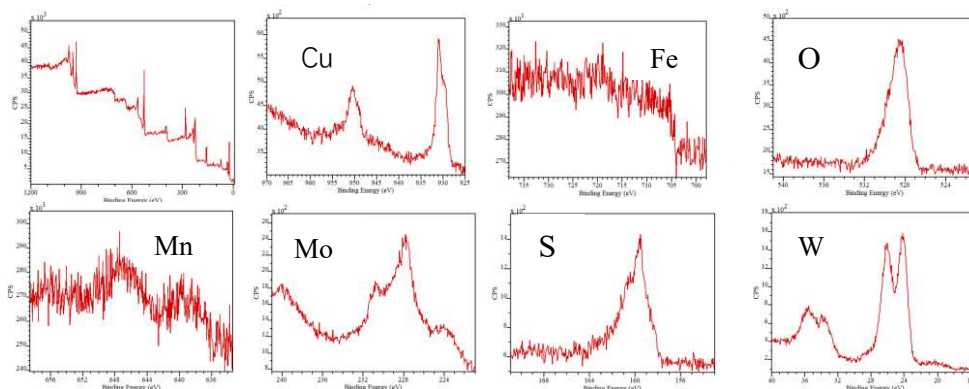


Fig. 6 XPS spectra of sample

The Fe 2p spectrum exhibits peaks at 710.8 eV (Fe 2p_{3/2}) and 724.5 eV (Fe 2p_{1/2}) with satellite features indicative of Fe²⁺. The Cu 2p spectrum shows Cu 2p_{3/2} and Cu 2p_{1/2} peaks at 932.5 eV and 952.3 eV, confirming Cu²⁺. The Mn 2p spectrum displays peaks at 641.2 eV (Mn 2p_{3/2}) and 652.8 eV (Mn 2p_{1/2}), characteristic of Mn²⁺. The W 4f spectrum exhibits a doublet at 35.4 eV (W 4f_{7/2}) and 37.5 eV (W 4f_{5/2}), while the Mo 3d spectrum displays peaks at 232.1 eV (Mo 3d_{5/2}) and 235.2 eV (Mo 3d_{3/2}), confirming W⁶⁺ and Mo⁶⁺. These results confirm that Fe²⁺, Cu²⁺, and Mn²⁺ randomly occupy the same crystallographic sites, Mo⁶⁺ and W⁶⁺ share the anion sites, and S²⁻ partially substitutes for O²⁻.

3.3 Optical properties

The optical properties of the HEFWOS nanosheets were investigated by UV-Vis-NIR spectroscopy (Fig. 7). The absorption spectra exhibit a broad and continuous absorption spanning

400–1400 nm, encompassing both NIR-I and NIR-II biological windows. Notably, no distinct LSPR peaks were observed, confirming the semiconducting nature of the material.

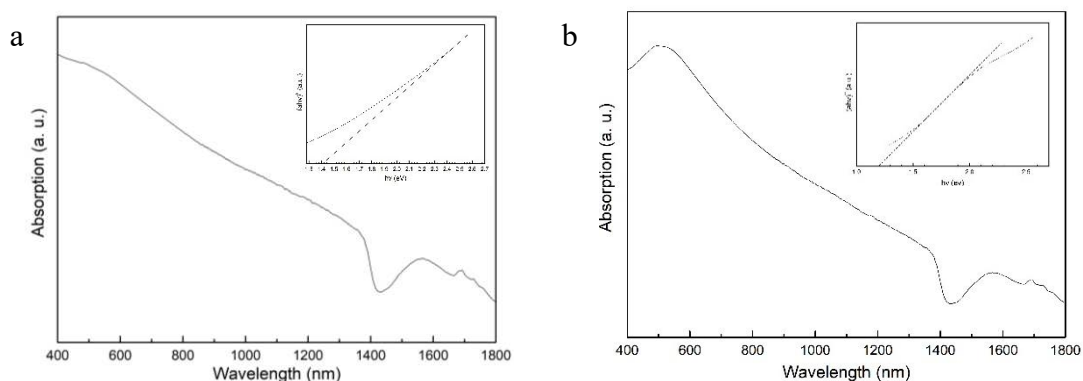


Fig. 7 UV-vis-NIR spectra of HEFMOs hydrothermally synthesized at 200°C for: (a) 4h, (b) 24h

The optical bandgap (E_g) was determined using the Tauc plot method for indirect allowed transitions:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g).$$

The bandgaps were estimated to be 1.42 eV (200 °C, 4 h) and 1.20 eV (200 °C, 24 h). The observed decrease in bandgap with prolonged reaction time is attributed to progressive sulfur incorporation and enhanced lattice relaxation. The high-entropy configuration plays a crucial role in modulating the electronic structure. The simultaneous presence of five metal cations with distinct electronic configurations (Mn: d^5 , Fe: d^6 , Cu: d^9 , Mo: d^0 , W: d^0) introduces a high density of electronic states near the band edges. Lattice distortion modifies crystal field splitting, forming intermediate bands that reduce the effective bandgap and extend absorption to longer wavelengths.

3.4 Photothermal performance

The photothermal conversion performance of HEFWOS-PEG was evaluated under NIR laser irradiation (Fig. 8). Upon irradiation with 808 nm, 976 nm, and 1064 nm lasers at $1.5 \text{ W} \cdot \text{cm}^{-2}$ for 5 min, the temperature of HEFWOS dispersions ($200 \mu\text{g} \cdot \text{mL}^{-1}$) increased by 38 °C, 28 °C, and 26 °C, respectively. Both the heating rate and maximum temperature exhibited concentration-dependent behavior ($50\text{--}200 \mu\text{g} \cdot \text{mL}^{-1}$), following the Beer-Lambert law. The wavelength-dependent temperature elevation correlates well with the absorption spectrum.

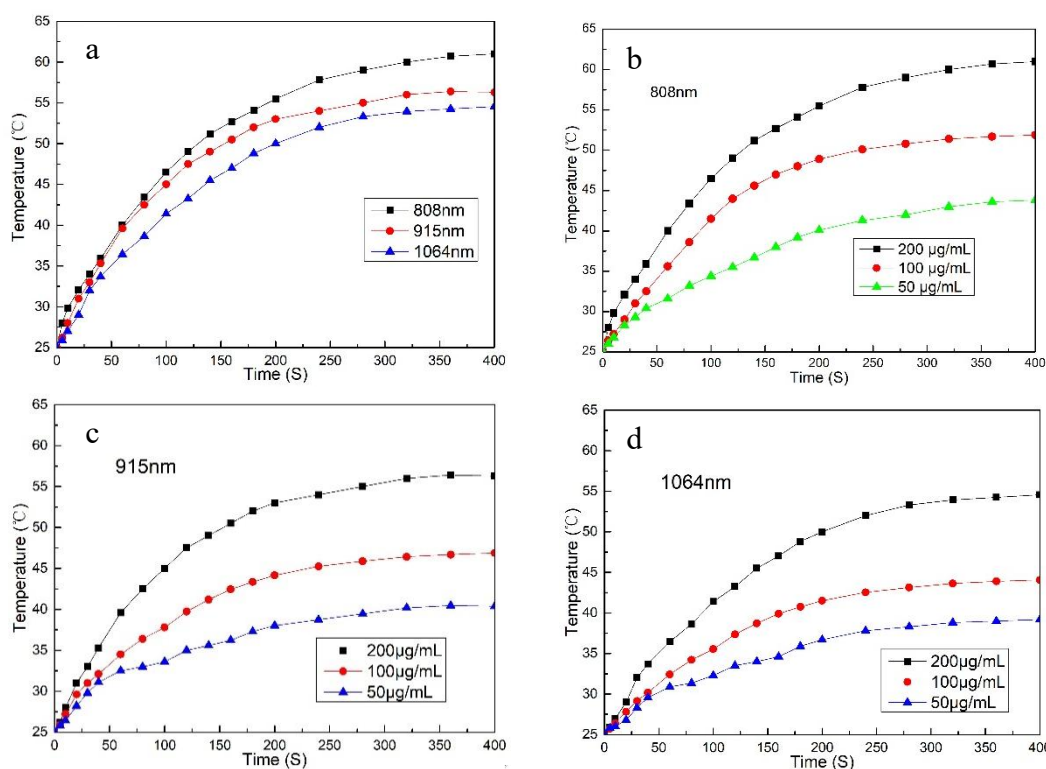


Fig. 8 Temperature changes of HEFWOs aqueous dispersions under irradiation of lasers (a) 808, 915 and 1064nm lasers, (b) with different concentrations at 808nm, (c) with different concentrations at 915nm, (d) with different

The sustained absorption in the NIR-II region is particularly advantageous for deep-tissue applications, where reduced scattering and absorption allow for deeper light penetration. The excellent photothermal properties and photostability confirm the potential of HEFWOS for photoacoustic imaging and photothermal therapy.

3.5 Magnetic properties and MR imaging

The magnetic properties of the HEFWOS nanosheets were characterized by VSM at room temperature (Fig. 9a). The sample exhibits a well-defined hysteresis loop with saturation magnetization (M_s) of 53.3 emu/g and coercivity (H_c) of 40.3 Oe, indicating soft ferromagnetic behavior. The high M_s is attributed to Fe^{2+} (d^6 , $S = 2$) and Mn^{2+} (d^5 , $S = 5/2$) ions through superexchange interactions via $\text{O}^{2-}/\text{S}^{2-}$ bridges. The low H_c facilitates easy magnetization/demagnetization for MRI applications.

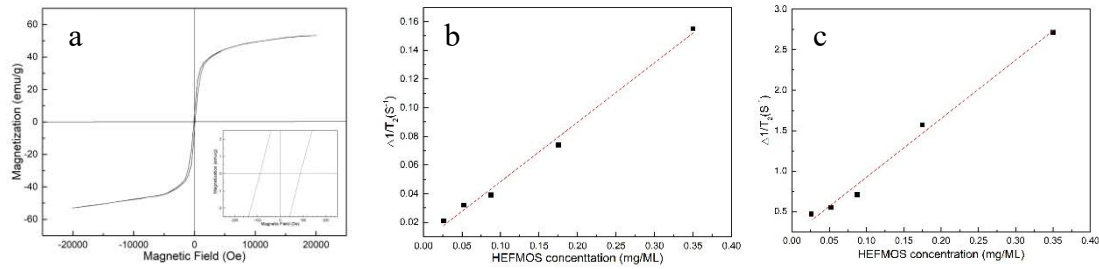


Fig. 9 (a)Magnetic hysteresis loops of HEFMOS measured at 300 K in the magnetic field range from 20 to 20 kOe, (b)The physicochemical characterization of HEFMOS T1-Weighted MR images of HEFMOS, (C)The physicochemical characterization of HEMOs T2-Weighted MR images of HEFMOS

The MRI contrast enhancement was evaluated using a clinical 3.0 T MRI instrument (Fig. 9b–c). Both T₁-weighted and T₂-weighted signal intensities exhibited concentration-dependent enhancement. The longitudinal (r₁) and transverse (r₂) relaxivities were calculated as 0.415 (mg·L⁻¹)⁻¹·s⁻¹ and 7.251 (mg·L⁻¹)⁻¹·s⁻¹, respectively, yielding an r₂/r₁ ratio of approximately 17.5. This dual-modal T₁/T₂ contrast capability arises from the synergistic contributions of Mn²⁺ (T₁ enhancement via dipole-dipole interactions) and Fe²⁺ (T₂ enhancement via local field inhomogeneities), uniformly distributed within the high-entropy lattice.

4. Conclusions

High-entropy (FeCuMn)(WMo)O_{4-x}S_x nanosheets with monoclinic structure (P2/c) were hydrothermally synthesized for the first time. Temperature governs phase purity: single-phase solid solution forms at 200 °C, while 140 °C yields CuFeS₂/MnWO₄ mixture. The high-entropy structure enables (i) broadband NIR absorption (400–1400 nm) with tunable bandgap (1.42→1.20 eV), (ii) efficient photothermal conversion (ΔT = 38 °C at 808 nm, 1.5 W·cm⁻²), and (iii) soft ferromagnetism (M_s = 53.3 emu/g, H_c = 40.3 Oe) with dual-modal T₁/T₂ MRI contrast (r₁ = 0.415, r₂ = 7.251 (mg·L⁻¹)⁻¹·s⁻¹). These properties position HEFWOS as a promising theranostic platform for NIR-I/II photothermal therapy and MRI-guided cancer treatment.

Acknowledgments

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