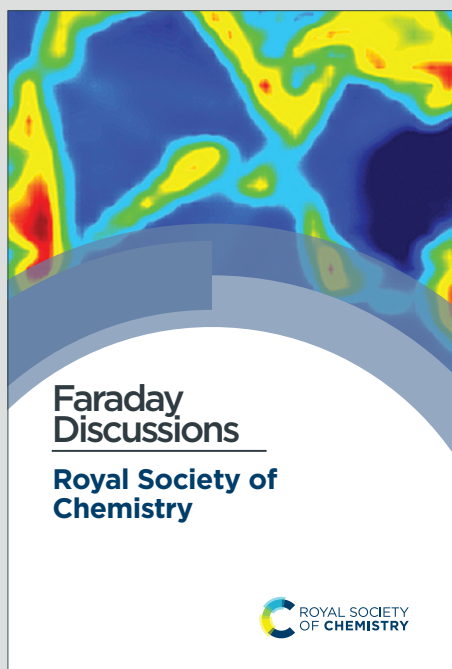


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Optical responses from High Entropy Alloys: experimental results and perspectives

Alexandre Nominé^{*a,b}, Alexander I. Solomonov^c, Juš Polanšek^b, Maxime Vergès^a, Yann Battie^d, Stéphanie Bruyère^a, Jaafar Ghanbaja^a, Jean-Francois Pierson^a, Janez Zavašnik^{b,e}, Michael Feuerbacher^f, Uroš Cvelbar^b, Thierry Belmonte^a, Valentin Milichko^{*a,g}

High-entropy alloys (HEAs) combine five or more elements in near-equiatomic ratios, opening an immense compositional space whose optical behaviour is still largely unknown. Phase-modulated ellipsometry on bulk CrMnFeCoNi (Cantor) shows that its intrinsic optical constants n , k , ε_1 , ε_2 deviate strongly from the arithmetic mean of the constituent elements—by up to a factor of two beyond 1 μm —yet the derived functional responses, reflectance R and absorption coefficient α , are reproduced to within $\sim 20\%$. Cantor nanoparticles have been produced by nanosecond electric discharges in liquid nitrogen. Dark-field spectroscopy and Mie calculations reveal a dominant scattering mode near 100 nm that red-shifts and broadens with increasing size; the steady-state photothermal rise calculated from absorption cross-section σ_{abs} falls between those of the constituent pure metals. Generalising the averaging rule, we compute proxy values of R and α for 10 994 density-functional-theory-predicted HEAs. Successive optical, thermal and resource filters condense the space to 58 candidates at 355 nm and eight refractory alloys at 1064 nm, illustrating a “sustainable-by-design” route for future HEA photonics.

Introduction

High entropy alloys (HEAs) emerged as a revolutionary class of materials in the early 2000s through the pioneering works of Yeh *et al.*¹ and Cantor *et al.*². Initially introduced as multi-principal element alloys containing five or more elements in near-equiatomic proportions, HEAs marked a paradigm shift from conventional alloy design, which typically focused on one or two principal elements with minor additions³. Even though the foundational premise of HEAs—that high configurational entropy could stabilize simple solid solutions despite significant atomic size differences and diverse elemental interactions—has been shown to be a simplistic framework^{4,5}, HEAs open unprecedented possibilities in metallurgical design.

The first decade of HEA research predominantly centred on mechanical properties, with extensive investigations into strength, ductility, hardness, wear resistance, and high-temperature stability⁶. These studies revealed exceptional combinations of properties, such as simultaneous strength and ductility, superior fracture toughness at cryogenic temperatures, and remarkable

radiation resistance, positioning HEAs as promising candidates for structural applications in extreme environments⁷. It was not until the 2010s that significant attention shifted toward the functional properties of HEAs. Researchers began exploring magnetic^{8,9}, catalytic¹⁰, hydrogen storage¹¹, thermoelectric¹², and radiation-resistant properties¹³, gradually expanding the application spectrum of these complex alloys. These functional properties exploration coincided with increasing capabilities to fabricate HEAs at the nanoscale, enabling entirely new application domains where surface area, quantum effects, and morphological control become critical design parameters.

The translation of HEA concepts to the nanoscale has presented both opportunities and challenges in materials science¹⁴. As revealed in recent comparative studies, HEA nanoparticle synthesis methods can be broadly categorized into top-down and bottom-up approaches, each with distinct advantages and limitations. Bottom-up synthesis techniques, including hot injection, carbothermal shock synthesis, and microwave heating, have demonstrated superior

^a Institut Jean Lamour - Univ. Lorraine / CNRS, Nancy, France

^b Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia

^c School of Physics and Engineering, ITMO University, St. Petersburg, Russia

^d Laboratoire de Chimie et Physique – Approche Multi-Echelle des Milieux Complexes - Univ. Lorraine, Metz, France

^e Max-Planck Society for Sustainable Materials, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

^f Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich, 52425 Jülich, Germany



process control and promote atomic-level mixing.

Recent studies by Dey *et al.*¹⁵ and Yang *et al.*¹⁶ have reported homogeneous elemental distribution through these approaches, while Qiao *et al.*¹⁷ achieved uniform ~12 nm particles using microwave heating with roll-to-roll compatibility. These methods generally favour compositional uniformity and offer potential for scalable production.

In contrast, top-down approaches such as pulsed laser ablation in liquids (PLAL) typically yield particles with broader size distributions (2–120 nm) with narrower distribution obtained by Waag¹⁸ and Löffler¹⁹ and may result in compositional heterogeneity or core-shell configurations. Nevertheless, as demonstrated by Tahir *et al.*²⁰, these methods can be cost-efficient when process parameters are optimised. Among the emerging synthesis routes, electric discharge in dielectric liquids represents a promising yet underexplored approach. This method combines aspects of plasma-based techniques with liquid-phase processing, potentially offering rapid quenching rates, precise compositional control, and ambient processing conditions without requiring vacuum systems^{21,22}.

Despite growing interest in HEA nanoparticles, their optical properties remain largely unexplored field in materials science. The current literature on HEA optical properties is sparse and fragmented across different compositions, morphologies, and spectral ranges, creating a significant knowledge gap for applications in light conversion, sensing, and photonics. Recent studies demonstrate that HEAs exhibit wavelength-dependent optical behaviours modulated by composition and microstructure. In the visible and near-infrared regions, optical responses have been observed in HEA thin films with structural phase variations and nanotwin features²³, while saturable absorption with modulation depths of 7.61% at 1 μm and 30.47% at 1.5 μm has enabled ultrashort fiber laser pulses²⁴. Deep-ultraviolet measurements on aluminium-rich alloys have revealed reflectance up to three times that of gold²⁵, supported by dielectric constant estimates from Drude/Lorentz models. In the terahertz domain, experiments on Nb–Mo–Ta–W thin films indicate high refractive indices that increase with film thickness, alongside rising extinction coefficients and conductivity²⁶. For bulk high entropy

borides, low thermal emittance (0.12) and solar absorption (approximately 0.4) have been observed over the 0.3–16 μm range²⁷.

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In contrast to conventional plasmonic/metallic nanoparticles, fundamental optical characterization data such as ellipsometry measurements and explicit scattering and absorption cross-sections of HEA remain largely unreported in the literature. This absence of comprehensive optical property data presents a significant barrier to the development of HEA nanoparticles for photonic and plasmonic applications. This study aims to address the critical knowledge gaps regarding optical properties of HEA nanoparticles. Specifically, we investigate the electric discharge method in dielectric liquids as a versatile approach for producing compositionally uniform HEA nanoparticles. Furthermore, we present a systematic characterization of their optical properties, with particular focus on light conversion applications through scattering and absorption mechanisms.

Methods

Nanoparticles synthesis and characterisation

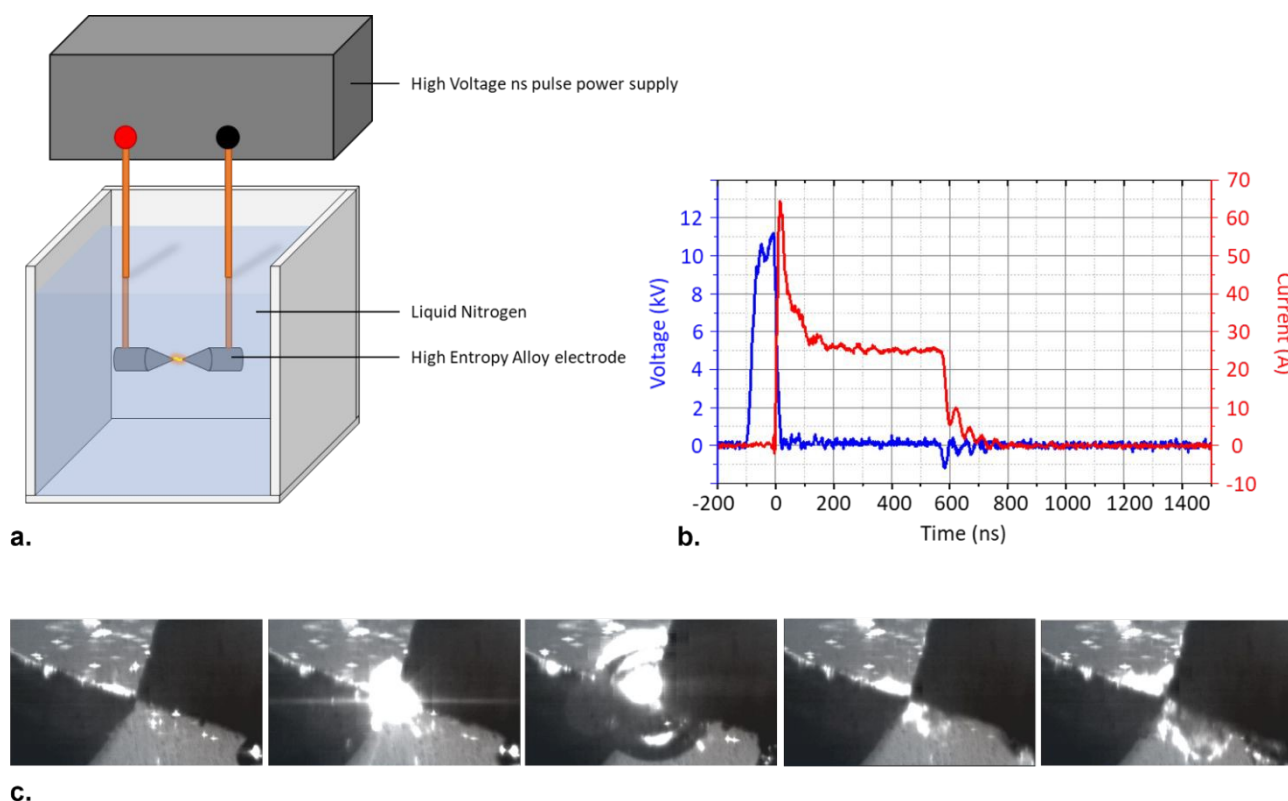
The high entropy alloy nanoparticles were synthesized using an electric discharge method in cryogenic dielectric liquids as previously described by Hamdan *et al.*²² in which different dielectric liquids have been tested: pure water, heptane and liquid nitrogen. Liquid nitrogen avoids high temperature oxidation during the process like for water or important carbon contamination like for heptane. The experimental setup consisted of a high DC voltage power supply (Technix SR15-R-1200, 15 kV–80 mA) connected to a solid-state switch (Behlke HTS-301-03-GSM), which delivered electrical pulses to one electrode, while the second electrode was grounded (fig 1a). This configuration produced a voltage rise time of 30 ns (fig 1b). Both electrodes were fabricated from a Cantor alloy ($\text{Fe}_{23.8}\text{Co}_{22.8}\text{Cr}_{22.3}\text{Mn}_{12.0}\text{Ni}_{19.1}$) and arranged in a pin-to-pin configuration while immersed in liquid nitrogen, which served as the dielectric medium. The characterisation of the Cantor Alloy is available in Ledieu *et al.*²⁸.



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Figure 1: Experimental setup and discharge dynamics for HEA nanoparticle synthesis via electric discharge in liquid nitrogen. (a) Schematic of the pin-to-pin electrode configuration with high voltage pulse power supply and liquid nitrogen medium. (b) Voltage (blue) and current (red) profiles during a discharge event, showing rapid rise time of 30 ns. (c) High-speed camera sequence (30,000 fps) capturing plasma ignition between electrodes followed by vapor bubble formation, expansion, and collapse within tens of microseconds.

The discharge dynamics were captured using a high-speed camera (FASTCAM SA5 model 1000K-M3) *al.*²⁹ recently predicted thousands of possible HEAs stable at 0.9 Tm, yet many of them become metastable



operating at 30,000 images per second. As illustrated in Figure 1c, the sequence reveals the temporal evolution of the discharge process. Initially, intense plasma ignition occurs between the electrodes, generating a bright emission zone. This is rapidly followed by the formation of a vapor bubble that expands outward from the discharge channel. The bubble continues to grow until reaching a maximum size, after which it undergoes collapse and subsequent oscillations. This entire cycle of bubble expansion and contraction occurs within a few tens of microseconds after the termination of the electrical discharge, as correlated with the voltage and current profiles shown in Figure 1b. These rapid thermodynamic changes in the vicinity of the plasma channel create extreme synthesis conditions that facilitate the formation of HEA nanoparticles. Chen *et*

at room temperature. The ultrafast quenching rates inherent to plasma discharges limit atomic diffusion and prevent the system from reaching the equilibrium multiphase state dictated by thermodynamics. Instead, they open a kinetic pathway in which metastable solid solutions can nucleate and grow, consistent with the “metastability window” described in classical continuous-cooling diagrams and illustrated by Yao *et al.*¹⁰ for HEA nanoparticles. This underscores the potential of non-equilibrium processes³⁰ such as plasma, laser or ultrasound to access nano-HEAs that cannot be obtained under equilibrium conditions.

The nanoparticles generated during the discharge process were collected via sedimentation onto a silicon wafer positioned at the bottom of the Dewar vessel.



After the complete evaporation of the liquid nitrogen, the particles were transferred to carbon grids for subsequent analysis by gently rubbing the silicon surface. The morphological, structural, and compositional characterization was performed using high-resolution transmission electron microscopy (HRTEM) on a JEOL ARM 200F cold field emission gun TEM/STEM operating at 200 kV with a point resolution of 0.12 nm. The microscope was equipped with a GIF quantum ER model 965 for enhanced imaging capabilities. Additionally, high-angle annular dark-field imaging in scanning TEM mode (HAADF/STEM) was combined with two-dimensional elemental mapping using energy-dispersive X-ray spectroscopy (EDX) to analyse the chemical composition and elemental distribution within the synthesized nanoparticle

Ellipsometry

Ellipsometric spectra for bulk HEA were acquired using a phase-modulated ellipsometer (UVISEL, HORIBA) at incidence angles of 50° and 70° across the 270–2100 nm spectral range. The measurement provides two ellipsometric parameters, ψ and Δ , at each wavelength. These parameters correspond directly to the ratio ρ between the Fresnel reflection coefficients r_p and r_s :

$$\rho = \frac{r_p}{r_s} = \tan(\psi) e^{i\Delta}$$

For the analysis, the HEA surface was considered sufficiently thick and opaque to be modelled as a semi-infinite medium. Under this assumption, the complex dielectric function (ϵ) of the material can be determined using the following equation:

$$\epsilon = \sin^2(\theta) \left(1 + \left(\frac{1 - \rho}{1 + \rho} \right)^2 \tan^2(\theta) \right)$$

here θ represents the angle of incidence. From this equation, both real and imaginary components of the complex dielectric function are determined (figure 2c and d).

Optical Dark-field

Optical resonances of individual HEA nanoparticles were characterized using white-light scattering

measurements in confocal dark-field configuration. Sample preparation involved depositing a solution droplet onto a fused-silica substrate and allowing the solvent to evaporate, resulting in isolated nanoparticles with a low surface density (approximately 0.1 particle/ μm^2). The measurements utilized a custom-built dark-field setup³¹ where s or p-polarized illumination from a halogen lamp source (HL-2000-FHSA) was directed onto the sample at a 65° angle relative to the substrate normal. The scattered light was collected using a Mitutoyo M Plan APO NIR 50 objective with a numerical aperture of 0.45. Spectral analysis was performed using a Horiba LabRam HR confocal spectrometer equipped with a cooled Andor DU 420A-OE 325 CCD camera and a diffraction grating featuring 600 grooves/mm.

Results

Optical properties of High Entropy Alloys

The optical properties of the equiatomic CrMnFeCoNi Cantor alloy were measured across the 200–2000 nm spectral range and compared with both its constituent elements and their arithmetic average. As shown in Figure 2, the Cantor alloy exhibits typical optical behaviour of metals characterized by a relatively high refractive index, significant extinction coefficient, negative real part of dielectric permittivity in the visible-NIR region, and strong absorption. In more details, Figure 2a reveals that the refractive index (n) of the Cantor alloy significantly deviates from the average of its constituent elements, particularly at longer wavelengths. In the infrared region (>1000 nm), the measured refractive index reaches values exceeding 5.5, substantially higher than both the individual metals and their average (approximately 3.5). Similarly, the imaginary part of the dielectric function (ϵ_2) shown in Figure 2d demonstrates considerable deviation from the average value, with the experimental curve displaying nearly twice the magnitude of the arithmetic mean in the near-infrared region. This deviation from the averaging is more limited in the case of the extinction coefficient (k) and the real part of the dielectric permittivity (ϵ_1) as illustrated in Figures 2b and 2c, respectively.



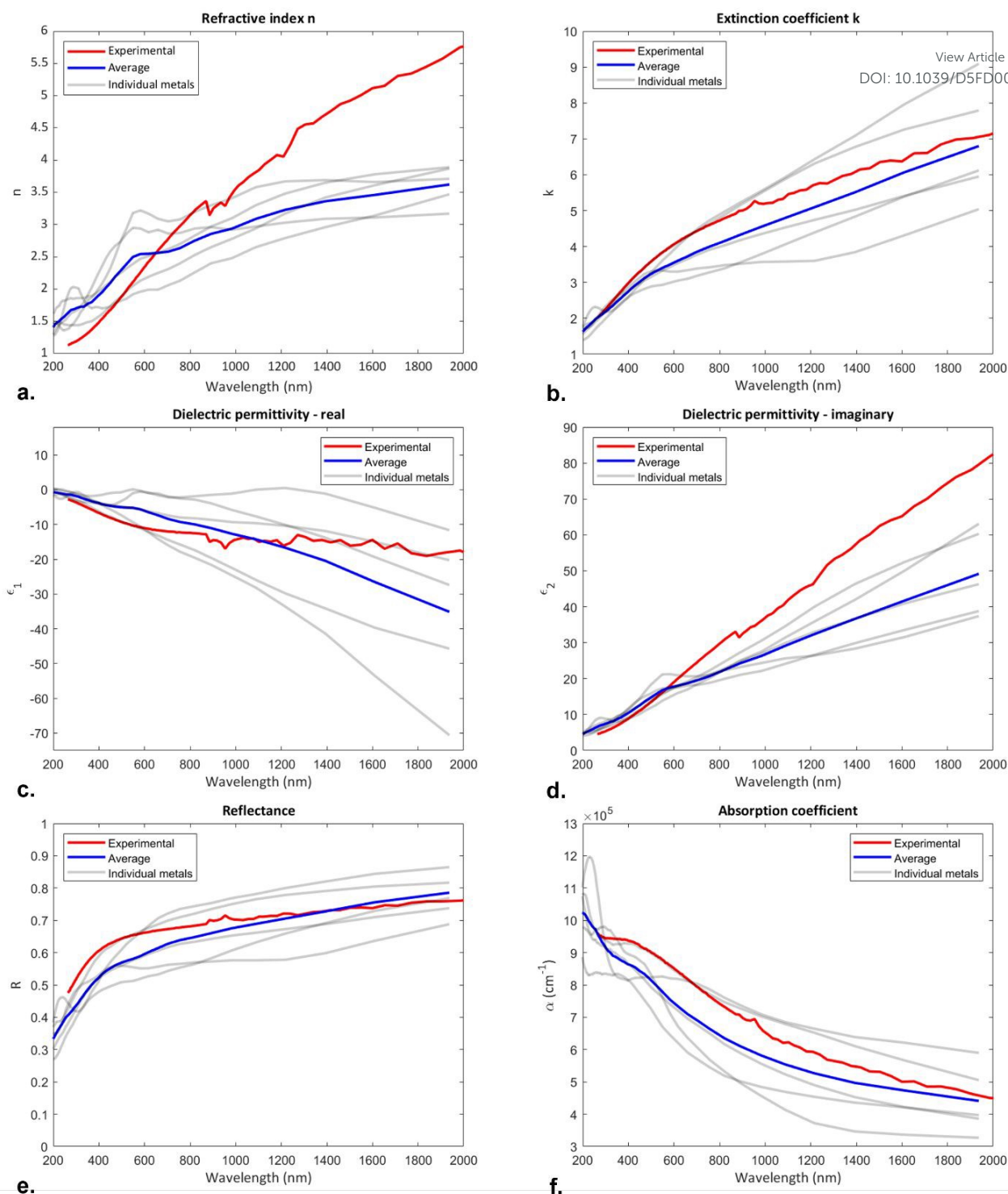


Figure 2: Optical properties of bulk equiatomic CrMnFeCoNi Cantor alloy compared to constituent elements. (a) Refractive index (n), (b) extinction coefficient (k), (c) real part of dielectric permittivity (ϵ_1), (d) imaginary part of dielectric permittivity (ϵ_2), (e) reflectance (R), and (f) absorption coefficient (α) as functions of wavelength across 200–2000 nm. Red curves represent experimental measurements of the Cantor alloy, blue curves show the arithmetic average of constituent elements, and grey curves correspond to individual constituent metals. Note the significant deviation of fundamental optical constants (n , ϵ_2) from averaging, particularly in the infrared region, while functional properties (reflectance, absorption coefficient) closely follow the arithmetic mean.

Interestingly, despite these significant deviations in fundamental optical constants, the functional optical properties like reflection (Figure 2e) and absorption coefficient (Figure 2f) demonstrate remarkably close agreement between the measured values and the average of the constituent elements. This surprising result suggests that while the intrinsic optical constants (n , k , ϵ_1 , ϵ_2) of high entropy alloys cannot be accurately predicted through the averaging, their macroscopic optical responses potentially could be.

Although the physics behind this observation requires some further study, a mathematical explanation could be proposed. We denote the alloy complex refractive index by $\tilde{n} = n + ik$, and the arithmetic average of the constituents by $\tilde{n}_{\text{avg}} = n_{\text{avg}} + ik_{\text{avg}}$. Writing the alloy values as deviations from the average ($n = n_{\text{avg}} + \delta n$, $k = k_{\text{avg}} + \delta k$), the Fresnel reflectance at normal incidence is:

$$R(n, k) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

A first-order Taylor expansion around $(n_{\text{avg}}, k_{\text{avg}})$ gives:

$$R \approx R_{\text{avg}} + \left. \frac{\partial R}{\partial n} \right|_{\text{avg}} \delta n + \left. \frac{\partial R}{\partial k} \right|_{\text{avg}} \delta k + O(\delta^2)$$

With $A = (n-1)^2 + k^2$, $B = (n+1)^2 + k^2$ the partial derivatives are:

$$\frac{\partial R}{\partial n} = \frac{2(n-1)B - 2(n+1)A}{B^2}$$

$$\frac{\partial R}{\partial k} = \frac{8nk}{B^2}$$

Evaluated at the average point, the linear correction depends on δn , δk . If linear averaging of (n, k) is exact, $\delta n = \delta k = 0$ and the first-order term vanishes. More

generally, because $R(n, k)$ is a smooth rational function, the error from using $(n_{\text{avg}}, k_{\text{avg}})$ is second-order in δ , which explains the close agreement seen for R and α compared to n and ϵ . For the absorption coefficient, $\alpha = 4\pi k/\lambda$, the first-order variation is simply $\delta\alpha = (4\pi/\lambda) \delta k$.

To test whether the Cantor behaviour is unique to that alloy or representative of a broader trend, we examined several binary alloys for which full optical constants are available in Refractiveindex.info open database³². Four alloys are chemically disordered solid solutions—Au–Ag³³, metastable Cu–Ag³⁴, Fe–Ni (80 % Ni)³⁵, and α -brass Cu–Zn³² (70–90 % Cu)—and two are ordered intermetallics, PtAl₂ and AuAl₂³⁶. The evolution of the absorption coefficient with the wavelength of all six binaries are plotted in Figure 3. The corresponding $n, k, \epsilon_1, \epsilon_2$ and R appear in the Supplementary Information. For Au–Ag (figure 3a) and Cu–Ag (figure 3b) the alloy curves lie entirely within the envelope defined by the two pure elements and shift smoothly toward the element that is enriched. The single Fe–Ni (figure 3c) composition fits the same envelope, suggesting the trend persists in this system. Cu–Zn (figure 3d) is less conclusive: its alloy spectrum sits closer to Cu than to Zn and shows no monotonic evolution, but the reports from which are extracted the optical constants lacks phase characterisation, so partial ordering cannot be ruled out.

The intermetallics behave very differently; both PtAl₂ and AuAl₂ (figure 3 e-f) plot far outside their elemental envelopes, confirming that long-range order introduces new electronic bands and invalidates any linear mixing law. Taken together—one HEA and six binaries—the data support the use of simple arithmetic averaging as a first-order proxy for the absorption coefficient and reflectance of disordered solid-solution alloys, while underscoring that it cannot be applied to ordered intermetallics.



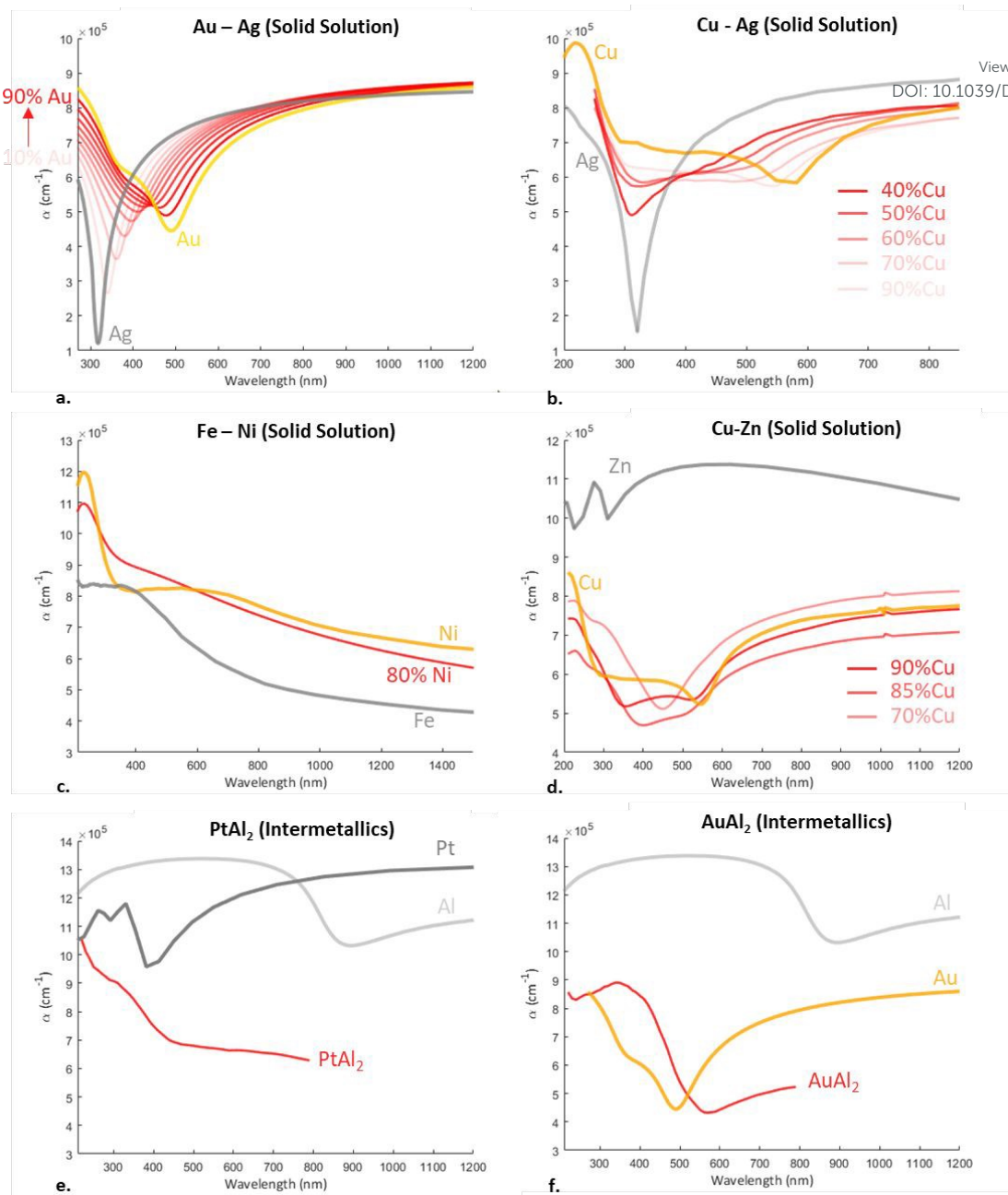


Figure 3: Absorption coefficient of several selected alloys (a) Au-Ag, (b) Cu-Ag, (c) Fe – Ni (d) Cu-Zn (e) PtAl₂ (f) AuAl₂

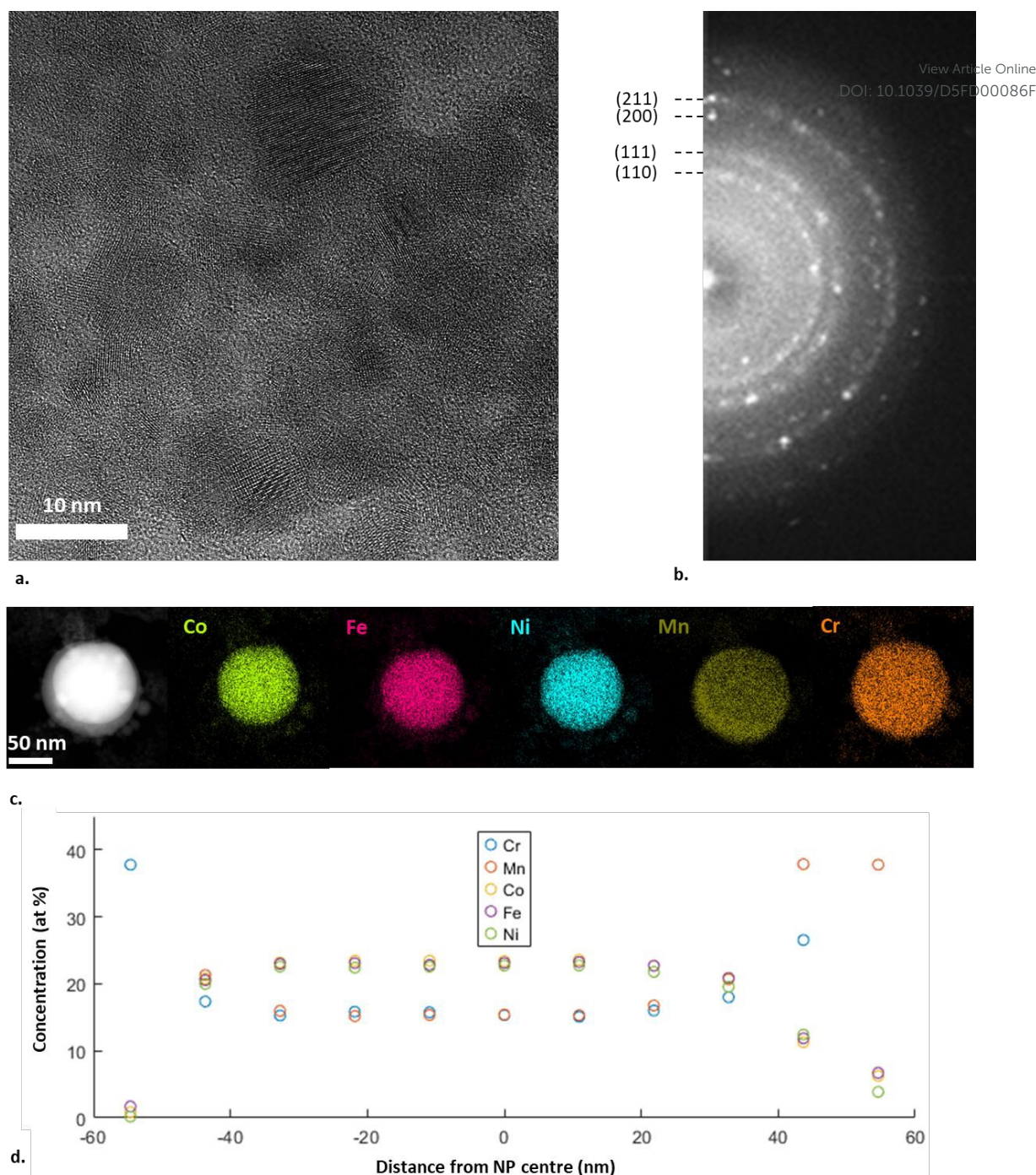


Figure 4: Structural and compositional analysis of HEA nanoparticles synthesized by electric discharge. (a) HR-TEM micrograph with magnified inset showing crystal lattice of smaller nanoparticles (scale bar: 10 nm). (b) Selected area electron diffraction pattern from multiple NPs with visible {110}, {111}, {200}, and {211} reflections, confirming face-centered cubic structure with lattice constant of ~360 pm. (c) HAADF-STEM micrograph with EDXS elemental mapping showing uniform distribution of all five constituent elements (Co, Fe, Ni, Mn, Cr) throughout a representative nanoparticle (scale bar: 50 nm). Elemental-line profiling over the Nanoparticle (d)

Transitioning from bulk properties to nanoscale synthesis, we investigated nanoparticles generated by the electric discharge method in liquid nitrogen. As

shown in Figure 4, the process produces CrMnFeCoNi high entropy alloy nanoparticles with diameters ranging from 10 to 500 nm. Electron diffraction analysis (Figure



4b) confirmed the crystalline nature of these nanoparticles, revealing a face-centred cubic structure with a lattice constant of approximately 360 pm, which closely matches that of the bulk Cantor alloy. Spatial distribution analysis of the chemical elements by energy-dispersive X-ray spectroscopy (Figure 4c-d) demonstrates that the composition of the nanoparticles remains close to that of the electrode material. It is worth noting that a few nm thick oxide shell of Mn and Cr is observed on the nanoparticles (figure 4 c-d) which is consistent with observation of other authors^{37,38}. This can be attributed to their brief exposure to atmospheric conditions during transfer to the TEM grid, rather than oxidation during the synthesis process itself. Elemental-line profiling (Fig. 4d) shows that the surface enrichment of Mn and Cr is balanced by a few-percent depletion in the particle core, but the overall composition remains close to the target. Such thin oxide

layers are common for metal nanoparticles and, given their small volume fraction, are not expected to perturb significantly the scattering signal. A quantitative assessment would require the wavelength-dependent optical constants of the mixed (Mn,Cr) oxide, which are not yet available; modelling the oxide contribution is therefore deferred to future work.

The optical properties of individual Cantor alloy nanoparticles were investigated using optical dark-field scattering spectroscopy. As shown in Figure 5a, the dark-field image reveals that HEA nanoparticles of different radii scatter light at different wavelengths, resulting in a variety of colours visible across the field of view. This multicoloured appearance suggests size-dependent optical resonances, a combined feature of plasmonic and high-refractive-index nanostructures.

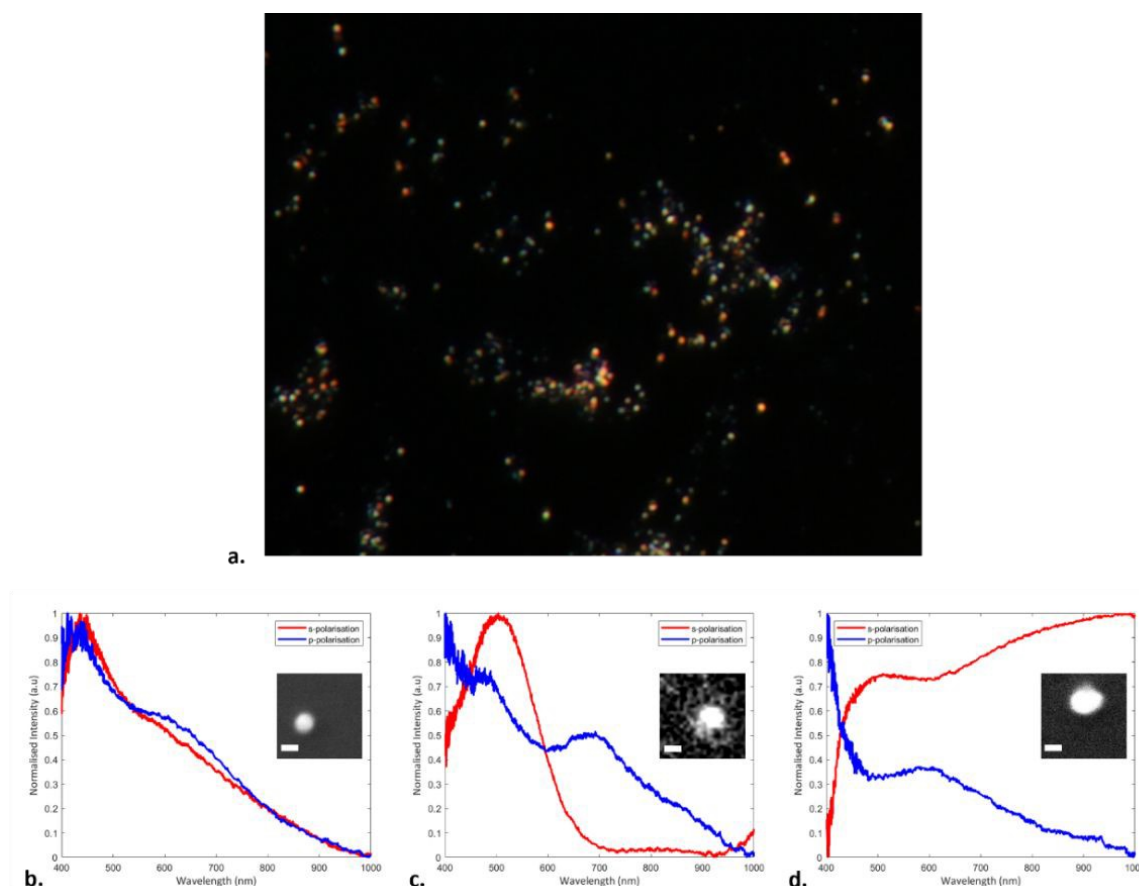


Figure 5: Dark-field optical characterization of individual HEA nanoparticles. (a) Dark-field microscopy image showing multi-coloured scattering from HEA nanoparticles of various radii. Polarization-resolved scattering spectra of particles with radii of (b) 115 nm, (c) 140 nm, and (d) 180 nm, revealing size-dependent optical responses. Red



and blue curves represent s-polarized and p-polarized illumination, respectively. Insets show dark-field images of the corresponding individual nanoparticles (scale bars: 100 nm).

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Polarization-resolved scattering spectra were collected from individual nanoparticles of different radii to quantify their optical response. Figure 5b presents the scattering spectrum of a 115 nm radius nanoparticle, showing relatively similar responses for s-polarization (red) and p-polarization (blue) illumination, with a gradual decrease in scattering intensity toward longer wavelengths. In contrast, the medium-sized particle (140 nm radius) shown in Figure 5c demonstrates strongly polarization-dependent scattering. Under s-polarized illumination, a pronounced peak appears around 500 nm, followed by a rapid decrease in intensity at longer wavelengths. While the p-polarized response shows a broader spectral distribution with a secondary resonance emerging around 750 nm, suggesting the excitation of higher-order optical modes. For the largest particle (180 nm radius) depicted in Figure 5d, the polarization dependence becomes even more pronounced. The s-polarized spectrum shows a significant red-shift with increasing intensity toward the near-infrared region. Simultaneously, the p-polarized response exhibits a complex spectral shape with multiple resonances across the visible range, followed by a gradual decrease in intensity beyond 700 nm. Such differences generally arise from a combination of factors: the influence of the silica substrate on the nanoparticle resonances, variations in nanoparticle radius, and differences in the experimental geometry for optical excitation and for collecting the scattered light within a limited solid angle.

To understand the underlying mechanisms of light interaction with HEA nanoparticles, we performed a calculation of the optical cross-sections across different radii using the experimental optical indexes represented in Figure 2. Figure 6 presents a comprehensive analysis of the scattering and absorption behaviours as a function of the nanoparticle size. Figures 6a-e show the evolution of scattering (σ_{sca}), absorption (σ_{abs}), and extinction (σ_{ext}) cross-sections for HEA nanoparticles ranging from 50 nm to 1000 nm in radius. For the

smallest particles ($R = 50$ nm, Figure 6a), the spectra exhibit characteristic Rayleigh scattering behaviour with cross-sections scaling as λ^{-4} , and absorption dominating over scattering. As the particle size increases to 100 nm radius (Figure 6b), we observe the emergence of spectral features associated with Mie scattering, including resonant peaks and a more complex wavelength dependence. At 200 nm radius (Figure 6c), distinct Mie resonances become prominent in the visible and near-infrared regions, with scattering now significantly exceeding absorption. This trend continues with further size increase to 500 nm (Figure 6d), where multiple overlapping resonances create a broader spectral response. Finally, at the micrometre scale ($R = 1000$ nm, Figure 6e), the nanoparticle enters the geometrical optics regime characterized by wavelength-independent cross-sections and predominantly forward scattering. Additionally, we illustrate in Figure 6f the electric field distribution around a 100 nm radius nanoparticle at 570 nm wavelength, displayed in two orthogonal planes. The XZ plane clearly reveals an electric dipole mode with strong field enhancement at the nanoparticle-air interface.

Quantitative agreement between optical models and experiments is hampered by substrate interactions and by the collection efficiency of the dark-field set-up. Nevertheless, both simulation and measurement concur on a key trend: the dominant scattering mode appears for particles close to 100 nm in diameter and then red-shifts while broadening as the particle radius increases.

The steady-state temperature rise ΔT of an isolated nanoparticle under continuous-wave illumination can be estimated from its absorption cross-section, σ_{abs} :

$$\Delta T = \frac{\sigma_{\text{abs}} I}{4\pi\kappa R}$$

With $\kappa = 0.0262$ - thermal conductivity of the surrounding medium (Air, 1bar, 300K) and I the irradiance set to $0.1 \mu\text{W} \cdot \mu\text{m}^{-2}$. Using σ_{abs} values



derived from Mie theory, we find that the temperature elevation predicted for the high-entropy alloy (HEA) particles lies between those calculated for the individual

constituent metals, consistent with their intermediate optical absorption (fig 6k).

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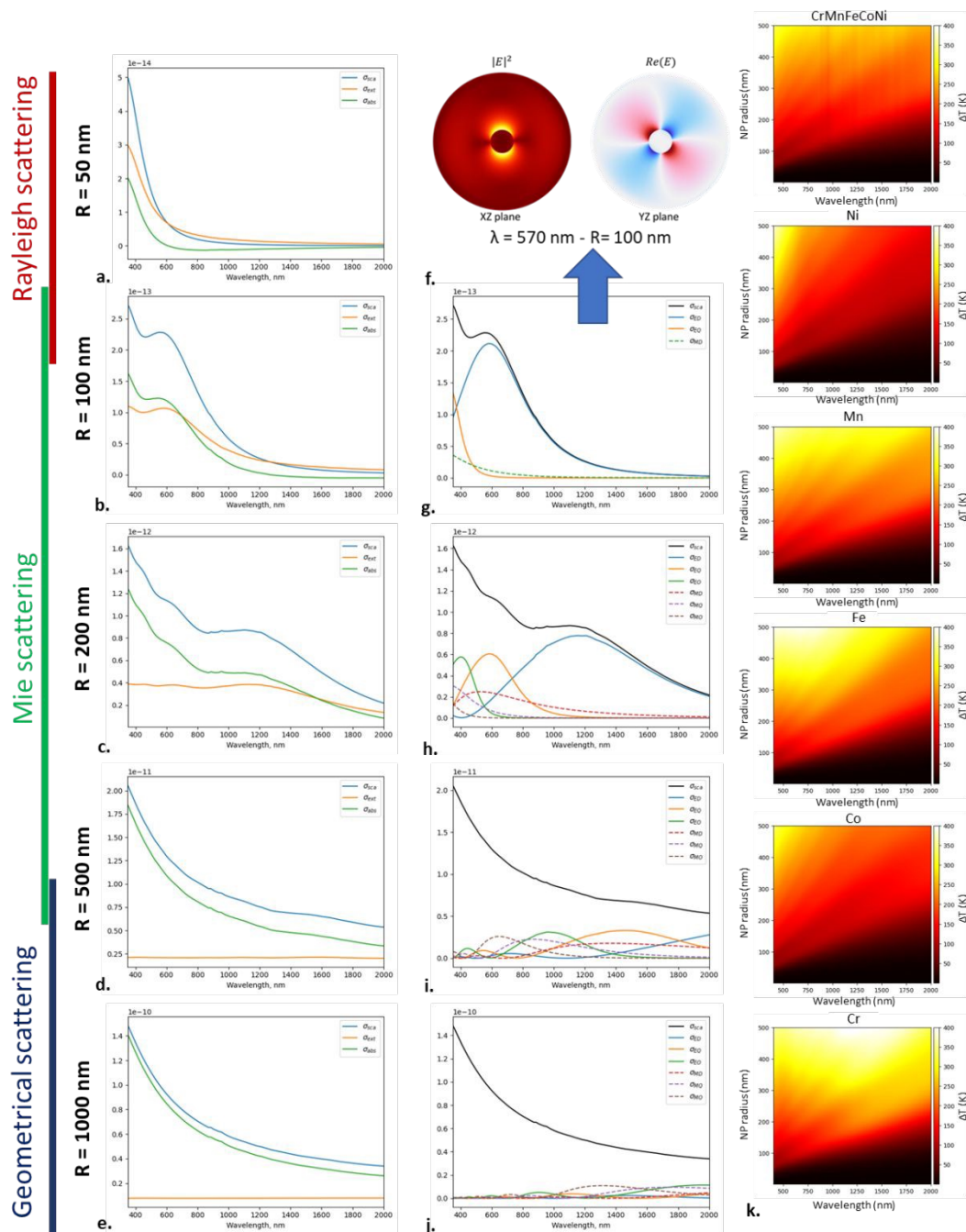


Figure 6: Calculation of optical cross-sections and field distributions for HEA nanoparticles of different sizes. (a-e) Evolution of scattering (σ_{sca} , blue), absorption (σ_{abs} , green), and extinction (σ_{ext} , orange) cross-sections for the nanoparticles with radii of 50, 100, 200, 500, and 1000 nm, showing transition from Rayleigh to Mie and then to geometrical scattering regimes. (f) Electric field distribution around a 100 nm radius nanoparticle at 570 nm wavelength in XZ and YZ planes, revealing dipole-like behaviour (g-j) Multipole decomposition of scattering cross-



sections for the nanoparticles of increasing size, showing contributions from various electric (a₂₂) and magnetic (a₂₁) modes. Temperature elevation of Nanoparticles as a function of their radius and the incident wavelength for an incident power of $I=0.1 \mu W/\mu m^2$ (k)

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Discussion and Perspective

High-entropy alloys (HEAs) have greatly enlarged the compositional landscape available to materials scientists, but the thermodynamic and property-governing principles that operate in this multidimensional space are still only partially understood. Between 2015 and 2018 several systematic surveys demonstrated that configurational entropy, S , is not by itself sufficient to stabilise single-phase solid solutions, contradicting the earliest HEA models^{4,5,39}.

These findings coincided with the emergence of data-driven materials science (e.g. Machine learning) and encouraged the use of computationally inexpensive descriptors (*aka* features) to navigate vast compositional space. In this context a feature is a physically motivated, rapidly calculated surrogate (proxy descriptor) for a more complex quantity; it need not be exact, but it must capture the dominant trend at a fraction of the cost of full thermodynamic or electronic-structure calculations. For instance, the most classical features are the average and standard deviation of quantities like atomic radius, electronegativity, Valence Electron Concentration (VEC) or melting point of the pure elements composing the HEA.

Following this approach and guided by the experimental study of the Cantor alloy, we adopt such a descriptor for optical screening. The results on figure 2 and 3, suggests that averaging the

absorption coefficient and the reflectance of the pure elements could be a first-principle proxy for the exploration of the optical properties of HEA. The proxy on the absorption coefficient of HEA - α^{HEA} - is defined as follow:

$$\alpha^{HEA}(\lambda) = \sum_i x_i \cdot \alpha_i(\lambda)$$

With x_i the atomic concentration of the element i within the HEA. Similarly, the proxy of the reflectance R^{HEA} :

$$R^{HEA}(\lambda) = \sum_i x_i \cdot R_i(\lambda)$$

To give a comprehensive overview of the possible optical properties of the HEAs the 40 elements palette selected by Chen *et al.* has been used. This represents $\binom{40}{5} = 658008$ possible equimolar alloys. The stability of the possible crystallographic phases has been modelled by DFT for all these combinations by the same authors. This has led to a subset of 30201 compositions for which single phase solid solution is stable at 0.9 Tm.

Within the 40 elements palette, the optical indexes could be found for 30 of them in Refractiveindex.info database³², which made it possible for calculate the absorption and reflectance proxy for 10994 alloys predicted as HEAs (fig 7).



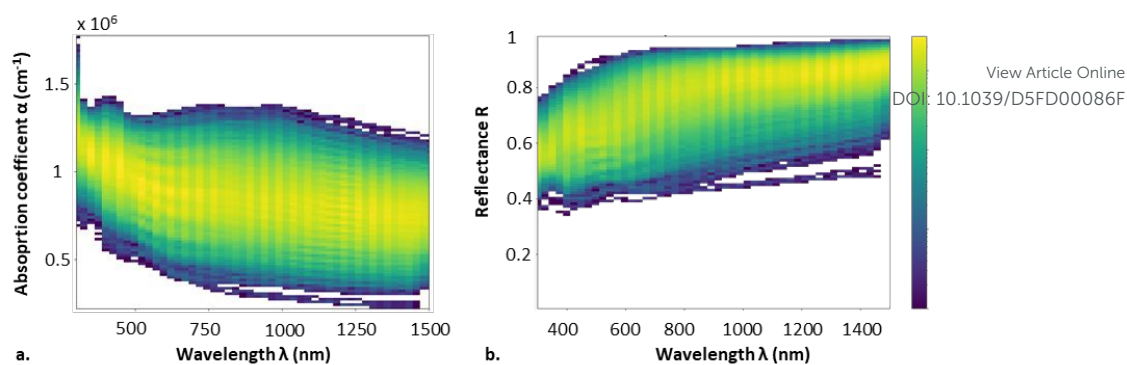


Figure 7: Calculation for 10994 HEA of the (a) absorption and (b) reflectance proxy within the 300 – 1500 nm spectral range

In sight of a possible application of HEA for high temperature optical applications (*e.g.* thermoplasmonics, photocatalysis), the absorption coefficient and the reflectance has been plotted with the average melting point at 355 nm (fig 8 a-b), 532 nm (fig 8 c-d) and 1064 nm (fig 8 e-f).

The absorption coefficients of HEAs stands within 0.75 to $1.3 \cdot 10^6 \text{ cm}^{-1}$ at 355 nm, 0.5 to $1.3 \cdot 10^6 \text{ cm}^{-1}$ at 532 nm, and 0.3 to $1.3 \cdot 10^6 \text{ cm}^{-1}$ at 1064 nm. The reflectance of HEAs stands within 0.4 to 0.8 at 355 nm, 0.4 to 0.9 at 532 nm, and 0.45 to 0.95 at 1064 nm.



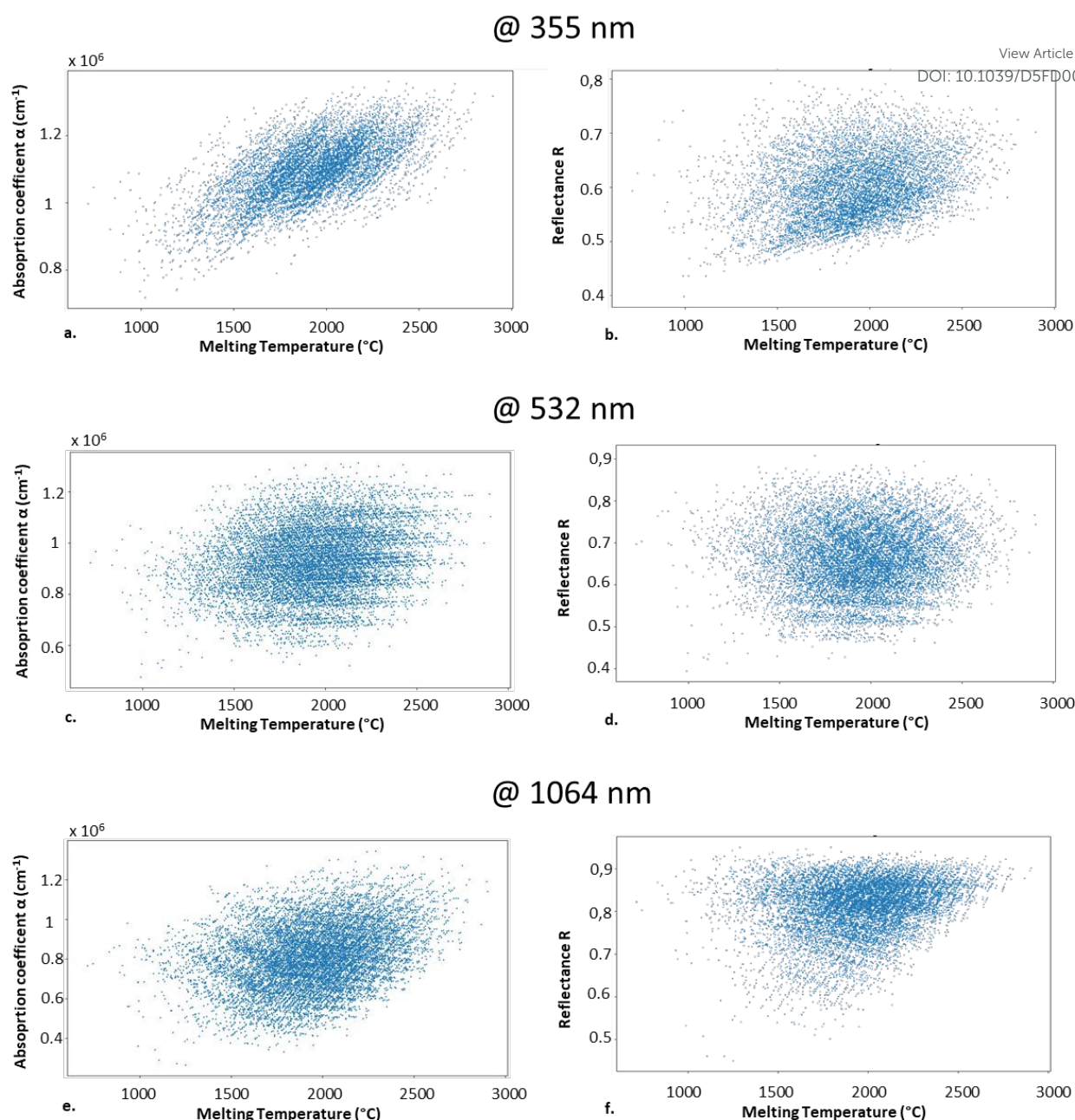


Figure 8: Absorption coefficient and reflectance of 10994 HEAs compared with the average melting point of their elements at 355 nm (a-b), 532 nm (c-d), 1064 nm (e-f)

In Figure 9, we showcase how these results could be used to identify regions of interest (ROI) to select the most promising subset of HEAs with an approach based on sustainable materials by design. This consists applying refining of possible candidates according to successive screening steps. The screening criteria are of three kinds: thermodynamics, physical properties and

sustainability. The selection from all the possible quinary alloys to the 30201 HEAs has been described in a previous section. Regarding the physical properties, three criteria have been successfully applied:

- **Absorption coefficient ($\alpha > 8.10^5 \text{ cm}^{-1}$):** 7717 HEAs satisfy this criterion at 355nm, 9248 at 532 nm and 5774 at 1064 nm.



- **Reflectance** filter has been set at 0.6 which is a moderate value that opens possibility for light to heat absorption. 4073 HEAs satisfies this second criteria at 355 nm and 809 at 532nm. This threshold had to be increased up to 0.8 for 1064 nm so that 129 HEAs could be kept.
- **Melting Point ($T_m > 2000^\circ\text{C}$):** this corresponds to the empirical definition of refractory alloys. In terms of application, this criterion overcomes largely the melting point of the most popular plasmonic materials ($T_m = 1064^\circ\text{C}$ For Au, $T_m = 961^\circ\text{C}$ for Ag, $T_m = 660^\circ\text{C}$ for Al) and of the typical photocatalyst TiO_2 ($T_m = 1843^\circ\text{C}$). This reduces the number of candidates to 1252, 362, 71 respectively at 355, 532 and 1064 nm.

Following a recent overview of sustainability of HEA⁴⁰, and in the perspective of an accelerated development of the alloys and the associated technology, we associated two sustainability criteria:

- **Maximal production (> 1kton/yr):** this measures the maximum production of each HEA based on the scarcest element of the alloy. Maximum annual production potential for each HEA is calculated using the formula:

$$P_{\max}^{\text{HEA}} = \min \left\{ \frac{P_i}{x_i^{\text{HEA}}} \right\}$$

where P_i is the global annual production of element i found in the US Geological Survey⁴¹, and x_i^{HEA} is the molar concentration of element i in the alloy. The threshold of 1000 tons does not necessarily mean that the targeted application will consume this amount. Indeed, conflict of use are also to be taken into account. A 1000 tons threshold allows the development of an application generating a demand of 50-100 tons per year with a reasonable risk of usage conflict. This drastically reduces the set to

157, 26 and 12 HEAs respectively at 355, 532 and 1064 nm.

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- **CO₂ Footprint (< 100kg.CO₂/kg):** The environmental impact of the metal extraction cannot be neglected in the life-cycle assessment of the products. Mass Carbon footprints f^{CO_2} per unit of mass of each metal m have been found in commercial GrantaEduPack© Software that gather different sources. Alternative open-access database has been published by Nuss *et al.*⁴² Carbon footprints have been converted into molar footprints f^{CO_2} . The footprints of the HEA j composed of n metals m in a concentration x have been calculated as follows:

$$f_{\text{HEA}}^{\text{CO}_2} = \sum_{m=1}^n x_m f_m^{\text{CO}_2}$$

- A threshold of 100 kg.CO₂/kg may sound excessive as compared to the one of the rock-forming elements like Iron (approx. 2kg.CO₂/kg) or Aluminium (8-12 kg.CO₂/kg). This remains however two orders of magnitude below the value for Gold and Platinum (30 – 60 tons CO₂/kg). This final criterion reduces the ROI to 58, 10 and 8 HEAs respectively at 355, 532 and 1064 nm. The list of HEA satisfying all the criteria are given in Supplementary Information.

This example shows how a succession of simple calculation helps to rapidly identify a few tens of HEA that could be of interest for a given set of properties. Indeed, the threshold could be modified upon the targeted application which would change the size and content of the ROI.

Such approach would be powerful to develop experimentally for two purposes:

- **Applicative:** This approach ensures a broad and exclusive screening of the field of



possible. Moreover, including sustainability, and particularly the resource availability avoids that costly research to be inapplicable as real-life products due to lack of resources. This filtering is not made at the expense of

the physical interest of the alloys since these criteria are applied first. Sustainability is potentially accelerating the larger scale deployment without being a limitation for fundamental investigations

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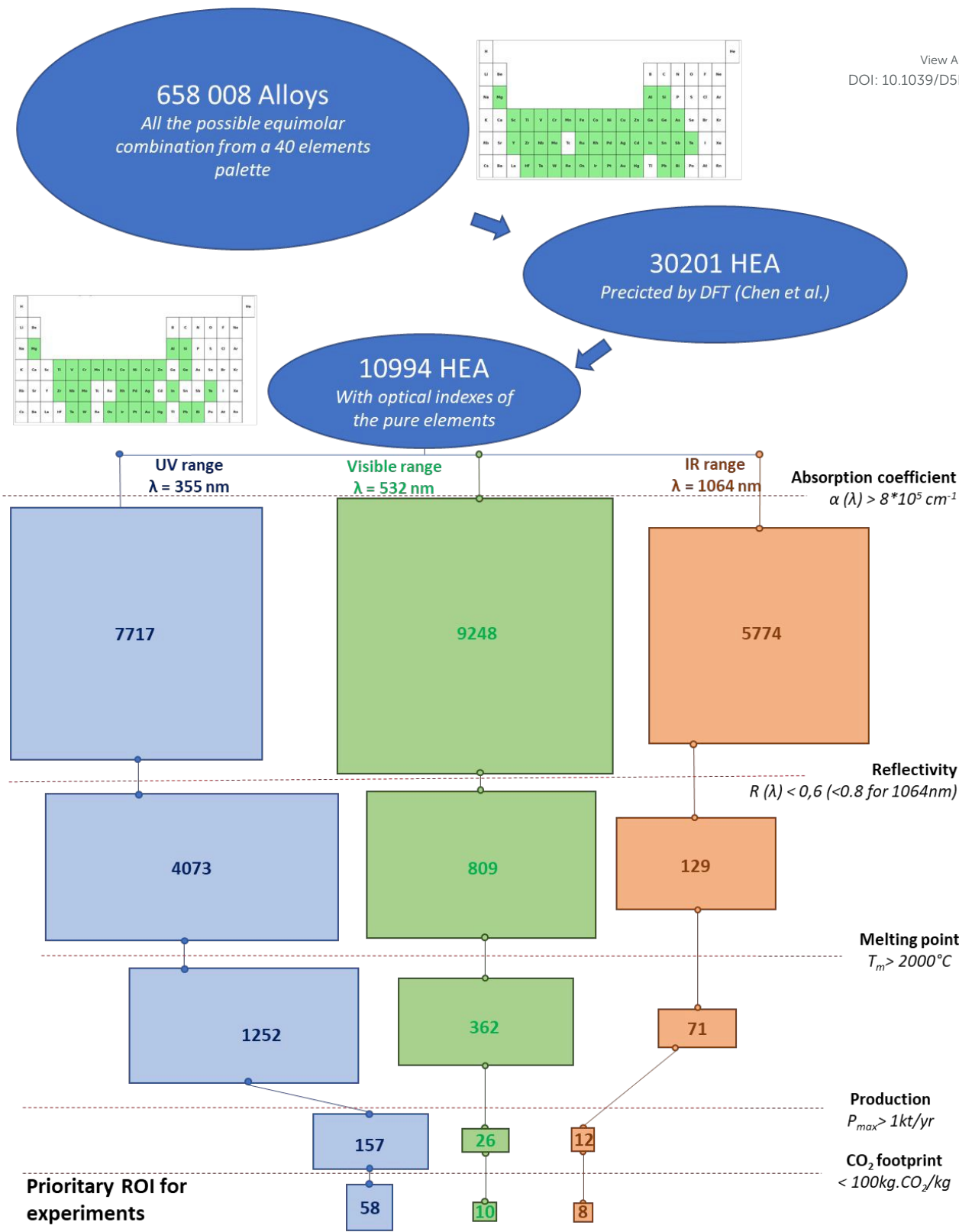


Figure 9: Overview of a *Sustainable Materials by Design* approach applied to sustainable HEA for optical applications



- **Fundamental:** as mentioned above, the definition of the descriptors (proxy) of the absorption coefficient and reflectance are based on observation on the Cantor alloy and not on a solid theoretical background. However, the measurement of the optical properties of HEA being too scarce, there is not yet alternative at low computational cost. Once a reasonable subset of HEA would have been characterized, this subset could be used to validate or update this approach with more accurate descriptors, and also inspire more theoretical works on the optical properties of solid solutions.

Conclusions

Bulk ellipsometry provides the first complete set of optical constants for the equiatomic CrMnFeCoNi (Cantor) alloy. Although n and k differ strongly from the arithmetic averages of the constituent elements, the functional quantities of practical interest—normal-incidence reflectance R and absorption coefficient α —remain within $\approx 20\%$ of the linear-mixing estimate from 300 to 1500 nm.

Nanoparticles generated by liquid-nitrogen electric discharge inherit these bulk constants, enabling a first calculation of optically induced heating. We find that the HEA photothermal response is bounded by those of its pure constituents.

Finally, the validated averaging rule has been applied to 10 994 DFT-stable HEAs. When combined with melting-point, production-volume and CO₂-footprint filters, the search space contracts to fewer than 60 promising compositions, illustrating how accurate bulk optics, photothermal estimates, and sustainability criteria can be integrated into a coherent “Sustainable materials-by-design” roadmap for future HEA photonic applications.

Author contributions

Conceptualization: **AN, VM** - Data curation: **AIS, MV, SB, JZ, YB, JG UC, TB, JP** – Investigation: **AN, VM, MV,**

SB, YB, JP, MF – Methodology: **AN, VM, YB, UC** - Writing – original draft: **AN, VM**, Writing – review & editing: **All authors** - Funding acquisition: **JFP, TB, AN, VM**

Conflicts of interest

There are no conflicts to declare

Data availability

Data are available in the depository mentioned in the data availability statement (DAS).

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Faraday Discussions Accepted Manuscript

Optical responses from High Entropy Alloy Nanoparticles synthesised by Electric Discharges in Dielectric liquid

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Alexandre Nominé^{*a}, Aleksander Solomonov, Maxime Vergès, Yann Battie, Stéphanie Bruyère, Jean-Francois Pierson, Janez Zavašnik, Uroš Cvelbar, Thierry Belmonte, Valentin Milichko

Data Availability Statement

Data for this article, including:

- High speed video recording of the dielectric discharge and bubble growth dynamics (**folder Discharge**)
- Optical properties of bulk equiatomic CrMnFeCoNi Cantor and individual metals - Refractive index (n), extinction coefficient (k), real part of dielectric permittivity (ϵ_1), imaginary part of dielectric permittivity (ϵ_2), reflectance (R), and absorption coefficient (α) as functions of wavelength across 200-2000 nm (**folder Optics bulk**)
- Transmission Electron Micrographs of nanoparticles (**folder Nanoparticles**)
- Scattering spectra of Nanoparticles (**folder Scattering**)

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