



## Fabrication of resonant high-entropy alloy nanospheres by the laser ablation technique

E.V. Gunina, A.O. Larin, P.N. Kustov, Alexandre Nominé,, J. Ghanbaja, S. Bruyere, Thierry Belmonte, D.A. Zuev

### ► To cite this version:

E.V. Gunina, A.O. Larin, P.N. Kustov, Alexandre Nominé,, J. Ghanbaja, et al.. Fabrication of resonant high-entropy alloy nanospheres by the laser ablation technique. 2022 Sixteenth International Congress on Artificial Materials for Novel Wave Phenomena (Metamaterials), IEEE, pp.X-250-X-252, 2022, 10.1109/Metamaterials54993.2022.9920910 . hal-04141041

**HAL Id: hal-04141041**

**<https://hal.univ-lorraine.fr/hal-04141041>**

Submitted on 26 Jun 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Fabrication of resonant high-entropy alloy nanospheres by the laser ablation technique

E.V. Gunina<sup>1</sup>, A.O. Larin<sup>1</sup>, P.N. Kustov<sup>1</sup>, A. Nomine<sup>2</sup>, J. Ghanbaja<sup>2</sup>, S. Bruyere<sup>2</sup>, T. Belmonte<sup>2</sup> and D.A. Zuev<sup>1</sup>

<sup>1</sup>ITMO University, Department of Physics and Engineering, 197101, 49 Kronverkskiy av., St. Petersburg, Russian Federation

<sup>2</sup>University of Lorraine, CNRS, IJL, F-54000 Nancy, France  
d.zuev@metalab.ifmo.ru

**Abstract** – The search for new materials for plasmonics and nanophotonics is justified by the need to create miniaturized optical nanodevices with unique properties in one nanostructure. High-entropy alloys have many material properties due to the peculiarity of the internal structure and multicomponent nature. These facts make such systems promising for nanophotonics. This paper presents the results of the experiments on the femtosecond laser ablation of a bulk material in an inert medium to create sphere-like nanoparticles of various sizes. Dark-field spectroscopy studies have demonstrated the presence of natural resonances in nanospheres, as well as their behavior with variation in the size of nanoparticles. We believe that the obtained results are perspective for creation of nanophotonic systems with extended functionality.

### I. INTRODUCTION

High-entropy alloys (HEA) appeared just over 15 years ago [1, 2, 3]. Nevertheless, thousands of papers on this topic have already been published (more than 5000 on the Web of Science database), and research and development is carried out in all economically developed countries. In many publications, the appearance of HEA is characterized as a big step forward in the development of metal alloys [4, 5].

A new class of materials has already found its application in mechanics [6] and catalysis [7] due to the incredible stability of the structure to high and low temperatures and an almost unlimited list of compositions, providing unprecedented possibilities for restructuring their physic-chemical properties. The fundamental difference between such alloys and other naturally occurring materials lies in the combination of a high degree of crystallinity, natural structural defects (vacancies, impurities, dislocations) with its chemical disorder. These materials are fundamentally significant due to the synergistic effect of combining chemical elements to demonstrate unique properties. Despite such a variety of properties, the methods for creating HEA nanospheres (NSphs) are rather limited, and the optical properties of such systems have been poorly studied.

Here, we considered laser ablation as a method for synthesizing NSphs while maintaining the properties of the starting materials, namely composition, crystal structure, chemical disorder and defects. We have demonstrated the presence of optical resonances and that they are consistent with the plasmonic nature of the constituent metal nanoparticles.

### II. RESULTS AND DISCUSSION

A high-entropy alloy target (Mn, Ni, Cr, Fe, and Co) was placed on the ITO and transferred to a chamber. There air was then pumped out and nitrogen supplied, thereby laser ablation was carried out in a nitrogen environment. The sample was ablated using femtosecond laser radiation (Pharos, Light Conversion), generating 200 fs pulses at a wavelength of 1030 nm (pulse energy 10 J). The average power at a maximum pulse repetition rate of 1 kHz is 0.1 W. Radiation was focused using a high-aperture objective (NA = 0.42). The formed objects remained on ITO for subsequent optical characterization.

It was shown that the fabrication method used makes it possible to create spherical nanoparticles in a quite wide range of sizes (see Fig.1(a)). Morphology of each NSph was checked with a scanning electron microscope



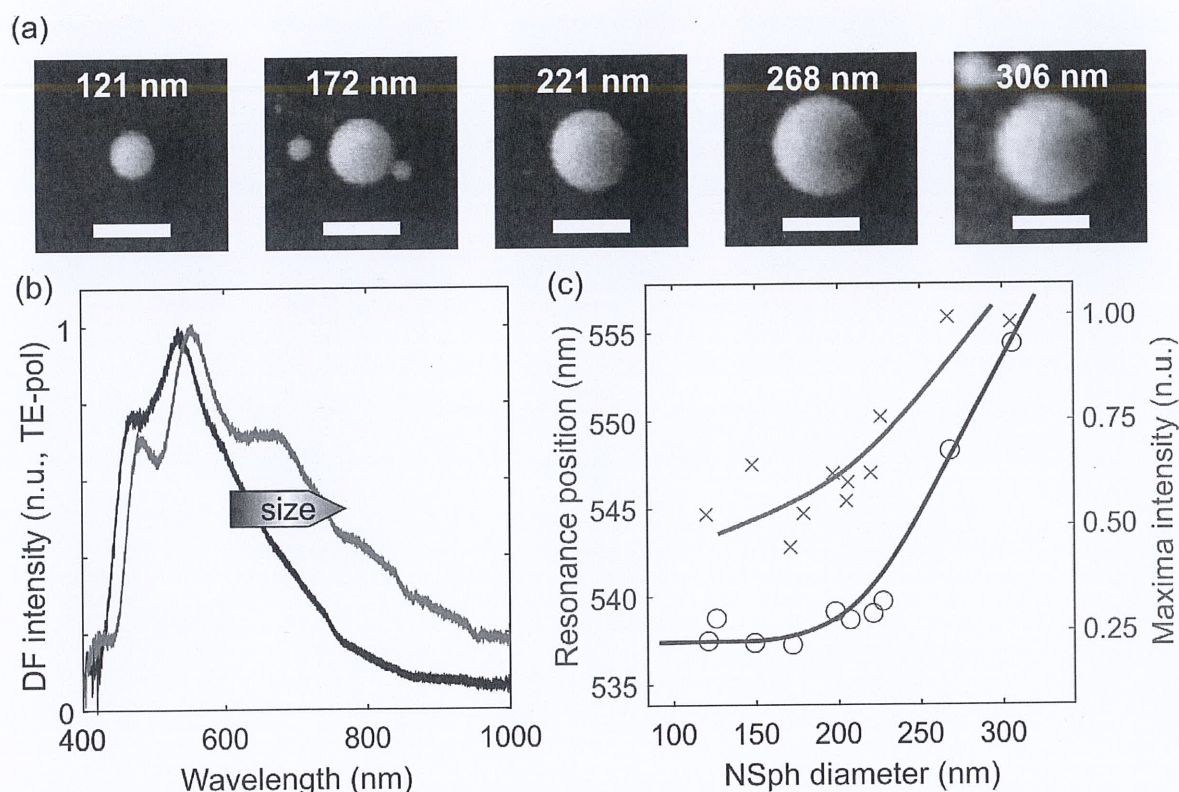


Fig. 1: Resonant optical properties of HEA NSPhs. (a) SEM image series of the HEA NSPh with variable size from 120 to 310 nm. Scale bars indicate 200 nm. (b) DF spectra of the HEA nanospheres on the ITO surface with diameter 150 (blue line) and 310 (red line) nm. Numbers indicate NSph diameters for certain DF spectra. (c) Resonant position of the peak at DF spectra and their intensity on the NSph diameter.

(SEM, Carl Zeiss, Neon 40) with normal detection. HEA NSPhs obtained in this way have a maximum size on the order of hundreds nm, which is a necessary requirement for their use in nanophotonics and plasmonics. From the technology point of view, the existed methods of carbothermal synthesis make it possible to obtain only 10-20 nm of HEA NSPhs.

The linear scattering measurements were performed at the room temperature on a confocal microscope system, consisting of two optical channels. Dark field optical channel was set at 68° relative to the pump optical axes. The Mitutoyo Plan Apo Infinity Corrected Objectives were used to collect scatter light from the sample (NIR, M = x50, NA = 0.42). The Mitutoyo objective (M = x10, NA = 0.28) was used to focus the linear-TE-polarized excitation of the halogen lamp. The optical response of the system is spectrally analyzed using a monochromator (Horiba Jobin-Yvon LabRam HR800 with diffraction grating support of 150 lines per mm) and a water-cooled CCD detector (iDus DU420A-OE, Andor) in the optical range 400 – 1000 nm.

The results of linear scattering upon excitation by a linearly TE polarized wave are shown in Fig.1(b). The size of spherical particles corresponds to the case of Mie scattering. This leads to the assumption of the existence of intrinsic resonances, the maxima of which are located in the visible wavelength range and the value of which directly depends on the size of the nanosphere. The experimental scattering spectra have resonant peaks in the visible wavelength range; the width of the considered lines is relatively large, which can be comparable with the case of large metallic nanospheres. It was noted follow behaviours with an increase in the size of the NSPhs: (1) red shift of the resonance peaks, (2) an increase in the intensity of the scattered light, (3) appearance of new resonances in the long-wavelength part of the spectrum (see Fig.1(b)). It is consistent with the ideas of the Mie theory. To study in detail the behavior of resonant peaks with increasing size, the position of the brightest peak at 540 nm was studied. The experimental results showed a relatively small but observable red shift (see Fig.1(c)).

### III. CONCLUSION

In this work we demonstrate results of fabrication and experimental studies of metallic NSphs made of high-entropy alloy materials (Mn, Ni, Cr, Fe, and Co). Investigation of fabricated system by the scanning electron microscopy shows that method produces spherical-shape nanoparticles with variable size, that is needed to support Mie resonance in NSphs. Results of experimental dark-field spectroscopy demonstrate that NSphs support resonances in the visible wavelength range and quite sensitive to the NSph diameter. Creation on the basis of such alloys of multi-functional, nonlinear, tunable elements of sensory, catalysis, transmission and processing of information.

### ACKNOWLEDGEMENT

This work is supported by the Russian Foundation for Basic Research (21-52-15029).

### REFERENCES

- [1] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau and S.Y. Chang, "Nanostructured high-entropy alloys with multiple principal elements: Novel design concepts and outcomes," *Adv. Eng. Mater.*, vol. 6(5), pp. 299–303, 2004.
- [2] Cantor B., Chang I.T.H., Knight P. and Vincent A.J.B., "Microstructural development in equiatomic multicomponent alloys," *Mater. Sci. Eng. A*, vol. 375–377, pp. 213–218, 2004.
- [3] Yeh J.W., Chen S.K., Gan J.Y., Lin S.J., Chin T.S., Shun T.T., Tsau C.H. and Chang S.Y., "Formation of simple crystal structures in Cu–Co–Ni–Cr–Al–Fe–Ti–V alloys with multiprincipal metallic elements," *Metal. Mater. Trans. A*, vol. 35A, pp. 2533–2536, 2004.
- [4] Yeh J.W., Chen Y.L., Lin S.J. and Chen S.K., "High-entropy alloys—a new era of exploration," *Mater. Sci. Forum.*, vol. 560, pp. 1–9, 2007.
- [5] Miracle D.B., "High entropy alloys as a bold step forward in alloy development," *Nature Communications*, vol. 10, pp. 1805, 2019.
- [6] Li Z., K.G. Pradeep, Y. Deng, D. Raabe and C.C. Tasan, "Metastable high-entropy dual-phase alloys overcome the strength–ductility trade-off," *Nature*, vol. 534, pp. 227–230, 2016.
- [7] Yao Y., Huang Z., Xie P., Lacey S.D., Jacob R.J., Xie H., Chen F., Nie A., Pu T., Rehwoldt M. and Yu D., "Carbothermal shock synthesis of high-entropy-alloy nanoparticles," *Science*, vol. 359, pp. 1489–1494, 2018.