

Spectral Physical Unclonable Functions: Downscaling Randomness with Multi-Resonant Hybrid Particles

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This paper presents a novel approach to optical PUFs using multiresonant gold-silicon particles with inherent nanoscale randomness, generating unique photoluminescence (PL) spectra that serve as unclonable keys. By leveraging random structural variations at the nanoscale, the proposed PUF design surpasses traditional, diffraction-limited methods. The authors demonstrate applications in secure labeling and all-optical one-time password tokens, showing promise for high-security applications in hardware cryptography, anti-counterfeiting, and access control. This approach potentially provides a new, multi-functional platform for security technology toward nanoscale-enabled unclonability, yet the reviewer has several questions regarding this paper.

- The title of this paper, "Spectral Physical Unclonable Functions: Downscaling Randomness with Multi-Resonant Hybrid Particles," raises some ambiguity regarding the precise meaning of "downscaling randomness." The only instance in the main text where the term "downscaling" is mentioned is in the phrase "downscaling critical PUF sizes beyond the optical diffraction limit," but the connection between this concept and randomness is not clearly established.
- This paper can be broadly divided into two parts: the fabrication of Au/Si nanostructures and the implementation of the PUF concept utilizing these structures. While femtosecond lasers are employed for fabrication, the rationale behind the choice of this light source is not clearly articulated.
- The discussion regarding the quantum efficiency (QE) of Au/Si nanostructures appears somewhat unclear. While the field enhancement factor is linked to the S-to-V value of the Au/Si particles, and the silicon grain size is fitted according to the KAMJ model, the resulting implications regarding the increase in the amount of amorphous silicon in determining QE are conflated. It would be beneficial to reorganize this section for better clarity and comprehension.
- In the reviewer's personal assessment, the robustness of the content in the PUF section appears to be weaker compared to the preceding discussion on the development of nanostructure fabrication processes. For instance, the data presented in Figure 4e seems to exhibit forms that are not commonly utilized in conventional PUF research. Fundamentally, an in-depth examination is needed to determine whether the PUF data utilized by the authors is genuinely random. For instance, while the current study extracts a set of five separate parameters from the PL data, it raises questions about whether these parameters can truly be considered distinct. In typical PUF research, a process is followed to verify the uniqueness and randomness of the key obtained, often through tests like the NIST randomness test to ensure that no intrinsic patterns exist. This study appears to lack such robustness. Additionally, the practice of varying polarization while collecting PL data for a single sample may pose similar concerns.
- In addition, while this study mentions the use of PDMS for encapsulation, additional testing is necessary to determine whether the PUF device can operate effectively under various environmental conditions, such as high temperature, humidity, etc.

Reviewer #2

(Remarks to the Author)

The authors utilize short annealing to generate Au-Si nanoparticles with random sizes and positions, applying these structures to the development of PL-based PUFs. After decomposing the PL characteristics of nanoparticle pairs into multiple parameters, they have designed the PUFs to achieve high encoding capacity. While the paper presents compact critical PUF sizes and adjustable security levels as unique features, several significant issues must be addressed before it is ready for publication. I would recommend a major revision.

1) Validity of the Process

1-1) The fraction of particles (or positions) with bright points appears to be quite low within each unit cell. If the unit cell is pixelated for encoding, the probability between "0" and "1" may not be equal. It is recommended to clarify whether this has been considered in deriving the PUF performance.

1-2) A more detailed explanation of the quantitative criteria used for extracting and encoding from collected signals is required. This includes the handling of variations in PL intensity of individual nanoparticles and the pixelation process for circular PL images from different positions.

1-3) Quantifying the unpredictability of the proposed PUF, including calculating information entropy, would provide essential support for the work.

1-4) Presenting a comparative list that indicates the performance level of the proposed PUF, such as the suggested $\sim 10^{54}$ of possible unique PUF labels and $\sim 10^{280}$ of encoding capacity, against other optical PUFs is recommended.

2) Reproducibility and Stability

2-1) Despite the absolute QE values ($\sim 1\text{--}3.5\%$) being presented, the QE range for each particle appears narrow. Providing insight into whether these can be distinguished within a meaningful resolution would strengthen the methodology.

2-2) The fabricated structure appears vulnerable to abrasion, especially considering the heavy reliance of the proposed authentication approach on information from individual particles. Presenting the stability of the proposed PUF under conditions such as wear and exposure to environmental factors would address this concern.

3) Minor Comments

3-1) On page 3, line 39, the authors emphasize the importance of nanoscale critical dimensions. Supporting this statement with additional references is suggested.

"Nanoscale physical unclonable function labels based on block copolymer self-assembly, Nature Electronics 5, 433-442 (2022)"

3-2) Specifying or visually representing the concepts corresponding to Challenge, Key, and Response would aid in comprehension.

3-3) Including brief explanations of newly introduced concepts such as forge-resistance would improve clarity.

3-4) Clarifying whether Weak PUF and Strong PUF are standard terms with quantitative criteria for distinction would provide valuable context.

3-5) On page 2, line 34, the manuscript does not clearly address whether the previously identified limitations of optical PUFs are effectively overcome in the proposed research.

3-6) Responses used for encoding (e.g., images of bright spots on the nanoscale, decomposed PL signals) seem to require specialized equipment or extended acquisition times. Offering a perspective on these points would be beneficial.

3-7) Describing the advantages of using an optical-based authentication method for OTP verification tokens would add depth to the discussion.

3-8) Addressing whether PL wavelengths from different particles with the fabricated nanoscale dimensions and structures remain consistent would clarify the reproducibility of the findings.

Reviewer #3

(Remarks to the Author)

This paper presents a novel optical Physical Unclonable function (PUF) that employs photoluminescence (PL) as the core mechanism for secure authentication. The approach generates unique, non-reproducible optical signatures through the random arrangement or structure of PL-emitting materials. These signatures function as challenge-response pairs (CRPs) within the PUF system, offering high entropy and ensuring the uniqueness and unpredictability of the responses. With carefully designed optical excitation and detection setups, the system achieves authentication using a large number of CRPs. The authors propose that this method provides a secure and robust solution for anti-counterfeiting applications.

While the optical PUF shows potential in generating high-entropy responses, its reliance on PL introduces significant challenges for practical implementation. PL-based systems demand precise excitation sources (e.g., specific wavelengths or intensities) and highly sensitive optical detectors to capture the emitted luminescence accurately. This requirement increases both the complexity and cost of deployment, limiting its suitability for large-scale or resource-constrained environments. Although various optical PUFs have emerged recently, real-world applications require simpler and more practical measurement methods. The mere use of complex equipment to achieve PUF functionality does not inherently justify the academic value of the approach.

Furthermore, the manuscript lacks sufficient detail on the number of CRPs that can be practically achieved. Another concern is the fabrication process, which involves fs-laser processing, contributing to high production costs. Given these factors, while the research may carry some scientific value, its utility as an optical PUF for practical applications appears limited.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The concerns raised in the previous round have been adequately addressed, and the revised manuscript shows significant

improvement. Therefore, I recommend its publication.

Reviewer #2

(Remarks to the Author)

The authors have adequately addressed the previous concerns. The revised manuscript is well-written and technically sound. I recommend accepting the manuscript for publication in Nature Communications.

Reviewer #3

(Remarks to the Author)

The revised version is well-written, and ready for publication.

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REPLY TO THE FIRST REVIEWER

We want to thank the Reviewer for their careful review and useful comments as well as positive evaluation of our manuscript. The detailed answers to all of their comments are presented below.

Comment 1. The title of this paper, "Spectral Physical Unclonable Functions: Downscaling Randomness with Multi-Resonant Hybrid Particles," raises some ambiguity regarding the precise meaning of "downscaling randomness." The only instance in the main text where the term "downscaling" is mentioned is in the phrase "downscaling critical PUF sizes beyond the optical diffraction limit," but the connection between this concept and randomness is not clearly established.

Our reply.

We thank the Reviewer for this valuable comment. Indeed, a more profound description of what is implied by the term "downscaling randomness" would make our concept much clearer for a Reader.

Spatial randomness as a general phenomenon may manifest itself in any system at multiple scales, from macro to micro, nano, and beyond. In the paradigm of physically unclonable functions, any system exhibiting spatial randomness can serve as a source of unique digital information, regardless of its characteristic size. For instance, consider a large room filled with different objects: this environment can be viewed as a physically unclonable system. The unique electromagnetic responses generated by the arrangement of these objects can be harnessed for integrity protection [1, 2]. Similarly, a handful of sand scattered uniformly on a table can also function as a PUF: every time a person creates such a system by throwing sand on the table, each time they will get a new, unique pattern. At smaller scales, one of the few industrial implementations of PUFs for anti-counterfeiting involves miniature (~1 cm) labels coated with hundreds of particles with sizes of ~100 microns [3]. And finally, most of the optical PUFs that can be found in literature exploit random systems with characteristic sizes of several microns or larger.

However, when speaking about PUF labels for anti-counterfeiting purposes, an additional criterion should be met for these systems (in addition to the randomness of their fabrication). And this criterion lies in the absence of alternative production technologies that could directly replicate any of the randomly obtained PUF labels. To illustrate this point, consider the previous example of a handful of sand randomly dispersed on a table. It is possible to replicate any specific sand pattern by painstakingly rearranging the sand particles with tweezers (or by automating this process using the developments of modern robotics and mechanics).

From this point of view, the majority of PUF labels proposed in recent years are, in fact, at high risk of being forged now or in the foreseeable future [4, 5]. This is due to the rapid advancement of various manipulation techniques capable of precisely moving single objects at the microscale [6-8]. Although the current high costs associated with these procedures may stop forgers from counterfeiting less expensive items, the need for a high-end, definitive solution is becoming increasingly relevant every year.

The logical solution to this problem would be reducing the critical PUF sizes (i.e., the characteristic sizes of spatial randomness in a PUF label that determine its unique response) down to the nanoscale. However, since the direct nanoscale measurements are hindered by the optical diffraction limit, this will greatly complicate and increase the cost of the PUF readout, which is counterproductive for industry applications.

In this work, we proposed the multi-resonant optical system (hybrid Au/Si particles) with nano-sized structural variations. We showed that this nanoscale *spatial* randomness translates into *spectral* randomness of each particle's photoluminescence, which can be easily measured by optical means. Although our measurements were constrained by the diffraction limit of the optical system employed, we found that each broadband PL spectrum may encode approximately 930 bits of unique spectral information (when using a machine-learning model to analyze PL spectra).

As a consequence, we decided to use the term “downscaling randomness” in the title of this paper for three main reasons:

1) First of all, in the given context, the word “randomness” refers specifically to the spatial randomness (in the internal structure of our Au/Si particles) that determines the unique PL responses of our PUFs.

Our manuscript includes transmission electron microscopy images of cross-sections of our Au/Si particles, which reveal structural variations with characteristic sizes on the order of 10–20 nanometers. Using a combination of theoretical considerations and numerical simulations, we demonstrated that it is these structural variations that greatly affect the form and shape of the resulting PL spectra. This fact emphasizes that we succeeded in downscaling (i.e., reducing) the critical sizes of our PUFs in comparison with the majority of earlier published PUF designs. To confirm this, we have compiled a comparative table that highlights recent related works, along with the characteristic sizes that influence the unique responses of the reported PUF labels (see Supplementary Table 3).

2) Secondly, we should note that there are several studies in the literature that have also explored the use of sub-microscale critical PUF sizes [4, 9-12]. Generally, these works introduce relatively large distributed systems characterized by nanoscale spatial features. To indirectly encode these features, authors typically employ mapping or imaging techniques of specific optical signals, where each pixel in the resulting map corresponds to the *integral* signal measured from a diffraction-limited area, usually around 1 μm^2 or larger. For instance, in ref 4, the authors presented self-assembled block copolymer *nanotemplates* from which they mapped the intensity of Raman scattering with a resolution as low as 0.75 μm^2 . They digitized the resulting maps,

encoding each pixel as either 0 or 1 based on its intensity value. In another study, Lapidis et al. [9] created plasmonic *nanojets* that exhibited different colors in the dark field microscopy due to the nanoscale variations in their geometry. The authors encoded these colors using their RGB values.

In these examples, as is common across other published PUF concepts, the amount of unique information derived from a single optical measurement (or, in other words, the number of degrees of freedom achieved through the encoding process) turns out to be *insufficiently small* compared to what is actually stored at the nanoscale. Consequently, a significant number of distinct PUF units may be misidentified as identical due to suboptimal reading/encoding protocols. Therefore, the critical PUF size as a performance parameter alone is not sufficient, and additional factors should be considered [12, 13]. Namely, we propose to use the concept of storage density, which is the amount of unique information extracted per unit area of a PUF label. The lower the PUF's critical sizes *and* the higher the entropy of measured PUF responses, the greater the storage density value will be. It can be argued that this parameter provides a more in-depth understanding of the PUF's performance than traditional measures such as encoding capacity [12, 13].

Within the concept of storage density, we believe that broadband photoluminescence of our hybrid Au/Si particles turns out to be extremely advantageous, as it bears a huge amount of information about the internal structure of our particles. To support this point, we have compiled the comparative table highlighting the value of PUF's storage density for recent related works (see Supplementary Table 3). Also, please see our estimations of storage density for all three proposed PUF models in Supplementary Note 16.

Therefore, our research not only reduces the critical PUF dimensions but also enhances the density of information stored within them (which can be viewed as *downscaling* the geometric dimensions of the "cells" that store individual random bits).

3) And finally, our work is organized in such a way that each subsequent proposed PUF protocol is built on smaller and smaller characteristic randomness sizes (and higher effective storing densities).

Indeed, our first PUF label model utilizes PL measurements with characteristic acquisition sizes on the order of 10 micrometers and has an effective storage density of 0.02 bit per square micrometer.

Our second PUF protocol revolves around computer-vision analysis of bright PL spots with characteristic sizes of 2-3 μm and has an effective storage density of 0.09 bit/ μm^2 .

Finally, our most beneficial PUF concept, which leverages the analysis of individual PL spectra featuring *nanoscale-enabled* spectral characteristics, achieves an impressive storage density of 3720 bits per square micrometer (which is at least 2-3 orders of magnitude greater than that of other PUFs presented in the literature).

In accordance with the Reviewer's comment, we modified the introduction as well as the discussion sections, adding the necessary information.

The following part is modified in the Introduction section:

"Here, we present novel optical PUFs based on multi-resonant gold-silicon (Au/Si) submicroparticles. Due to the specifics of their laser fabrication, these particles exhibit

*distinct intricate internal configurations, which inevitably affect their broadband photoluminescence (PL) spectra. We explore this structure-spectrum relationship and describe how truly random nanoscale variations in our particles' internal arrangement, coupled with strong optical resonances, give rise to the unique spectral features in their PL. We employ these optical responses as unclonable keys, which turns out to be extremely advantageous thanks to the huge amount of unique information contained in each PL spectrum. In contrast to typical PUFs that rely on directly encoded spatial randomness within the microscale dimensions, our spectrum-based concept allows downscaling critical PUF sizes beyond the optical diffraction limit. We develop several techniques for harnessing our spectral randomness, ranging from the most basic methods to more advanced and beneficial, and offer adaptable PUF-based security applications, including robust anti-counterfeiting labels (weak PUFs) and ML-driven OTP verification tokens (strong PUFs, see **Figure 1**)."*

The following paragraph is added to the Discussion section:

"One of the key aspects that distinguishes the presented work is our approach to addressing the structural variations in fabricated Au/Si particles. Since the direct analysis of this internal randomness (with characteristic sizes of 20 nm) requires tedious TEM-based techniques, we proposed using the particles' PL spectra as an alternative, highly capacious source of unclonable keys. In support of this method, we investigated how the multi-resonant nature of our particles establishes a strong linkage between their internal composition and the spectral features of the emitted PL. We have shown that each PL spectrum contains a wealth of unique spectral information, leading to an exceptionally high storage density (i.e., the amount of data extracted from a PUF per unit area). Indeed, in our latest protocol, which employs machine learning to encode individual PL spectra, each square micrometer of the label effectively stores 3,720 random bits (Supplementary Note 15). This represents an exceptional storage density that is 2-3 orders of magnitude greater than that of other optical PUFs (see the calculation of this parameter for all of the presented PUF concepts in Supplementary Note 16). Ultimately, the Supplementary Table 3 demonstrates that we have successfully downscaled the characteristic randomness of our PUFs."

Additionally, we created a new Supplementary Note 16 ("On the concept and calculation of storage density"), which includes our considerations on the concept of storage density, and Supplementary Table 3, which compares the essential parameters between our three PUF protocols and several other notable works.

References used in the answer:

- [1] Tobisch, Johannes, et al. "Remote inspection of adversary-controlled environments." *Nature communications* 14.1 (2023): 6566.
- [2] Wimmer, Lara, Eckhard Grass, and Ulrich Rührmair. "Monitoring of a local environment using a physical unclonable function." U.S. Patent Application No. 18/477,027.
- [3] Moscatelli A. *Physically unclonable functions fight forgery //Nature Nanotechnology*. – 2022. – T. 17. – №. 8. – C. 818-818.
- [4] Kim, Jang Hwan, et al. "Nanoscale physical unclonable function labels based on block copolymer self-assembly." *Nature Electronics* 5.7 (2022): 433-442.
- [5] Marakis, Evangelos, et al. "Clones of the unclonable: Nanoduplicating optical PUFs and applications." *arXiv preprint arXiv:2212.12495* (2022).

- [6] Gao, Dongliang, et al. "Optical manipulation from the microscale to the nanoscale: fundamentals, advances and prospects." *Light: Science & Applications* 6.9 (2017): e17039-e17039.
- [7] Fränzl, Martin, and Frank Cichos. "Hydrodynamic manipulation of nano-objects by optically induced thermo-osmotic flows." *Nature communications* 13.1 (2022): 656.
- [8] Zhou, Lei-Ming, et al. "Recent progress on optical micro/nanomanipulations: structured forces, structured particles, and synergetic applications." *ACS nano* 16.9 (2022): 13264-13278.
- [9] Lapidas, Vasily, et al. "Direct laser printing of high-resolution physically unclonable function anti-counterfeit labels." *Applied Physics Letters* 120.26 (2022).
- [10] Zhang, Tongtong, et al. "Multimodal dynamic and unclonable anti-counterfeiting using robust diamond microparticles on heterogeneous substrate." *Nature Communications* 14.1 (2023): 2507.
- [11] Zhang, Taiping, et al. "Random Nanofracture-Enabled Physical Unclonable Function." *Advanced Materials Technologies* 6.6 (2021): 2001073.
- [12] Wang, Kun, et al. "All-silicon multidimensionally-encoded optical physical unclonable functions for integrated circuit anti-counterfeiting." *Nature Communications* 15.1 (2024): 3203.
- [13] Smith, Joshua D., et al. "Plasmonic anticounterfeit tags with high encoding capacity rapidly authenticated with deep machine learning." *ACS nano* 15.2 (2021): 2901-2910.

Comment 2. This paper can be broadly divided into two parts: the fabrication of Au/Si nanostructures and the implementation of the PUF concept utilizing these structures. While femtosecond lasers are employed for fabrication, the rationale behind the choice of this light source is not clearly articulated.

Our reply.

We thank the Reviewer for this comment. Over the past two decades, laser-assisted fabrication has emerged as a powerful method, offering extensive fabrication possibilities due to their precise control over laser beam parameters and the irradiation modes applied to the sample surface. In particular, the femtosecond laser fabrication attracted a lot of interest thanks to the high precision, throughput and scalability of this technique [Optics & Laser Technology 135 (2021): 106687].

In our study, we employed fs-laser fabrication to locally initiate a variety of non-equilibrium thermo- and hydrodynamic relaxation processes. This included ultrafast thermal excitation of bi-layer Au/Si thin films, their partial ablation and melting, and the consequent launch of random hydrodynamic perturbations of the molten materials. Such an approach allowed us to successfully fabricate Au/Si microstructures characterized by a stochastic spatial distribution of hybrid particles, each exhibiting unique nanoscale structural variations, as presented in our findings.

From a practical standpoint, while the initial costs associated with fs-laser employment can be considerably high, the long-term benefits of our proposed fabrication method are quite promising. Indeed, our single-step, high-throughput fs-laser printing technique requires minimal additional consumables and is characterized by a long warranty period for the equipment used. Consequently, the primary contributor to the cost of our PUFs is the equipment expenses, which diminishes over time due to the long service life and mass production. To provide some evidence for this thesis, we have estimated the total cost of producing our PUF labels (see Supplementary Note 17). The obtained cost of approximately \$0.30 per each security label is acceptable, especially when compared to other PUFs documented in the literature (see Supplementary Table 3). This result suggests that fs-laser fabrication is indeed a viable option for practical applications.

To provide a Reader with these important points, we significantly modified the Discussion section of the manuscript as well as provided our fabrication cost estimations in the Supplementary Note 17 ("Calculation of the overall cost of a single PUF label"). Please, see below the part of the Discussion section that mentions the rationale behind our choice of fs-laser fabrication (green color highlights modifications of the text made).

... Considering the potential practical value of our PUFs, it is important to emphasize their key advantage: high-entropy spectral responses controlled by nanoscale structural randomness. This concept provides the highest level of protection, not only in the immediate future but also over many decades to come. This is particularly crucial as we enter an era where traditional PUFs, which rely on microscale

spatial randomness, will become increasingly vulnerable due to advancements in precise micro-manipulation techniques. Although in our approach demonstration we have used costly laboratory equipment, the long-term implementation will substantially reduce expenses for each individual PUF label (see Supplementary Note 17 for our cost estimations). Additionally, the rapid advancements in industrial fiber-optic fs-lasers and spectrometers are expected to further enhance the viability of our technology (for example, in Supplementary Note 18 and Supplementary Fig. 22 we showed that our PL measurement setup can be greatly simplified by employing a low-cost commercial spectrometer). Another important point is the environmental stability of our labels; when encapsulated in a polydimethylsiloxane (PDMS) protective layer, they demonstrate robust performance against a variety of typical external disturbances (see Supplementary Note 19 and Supplementary Figs. 23-24). With all of the above, we believe that our approach is going to find its industrial niche in the future.

In summary, we presented an original design concept of ultra-robust Physical Unclonable Functions using the relationship between nanoscale randomness and macroscale spectral characteristics. We chose multi-resonant Au/Si submicroparticles (500–900 nm), exploiting their unique PL response as a "fingerprint" of their internal structure with truly random compositional variations. ~~To create these particles, we adopted a single-step laser-induced fabrication technique, providing scalability and high throughput.~~ To create these particles, we used fs-laser excitation of thin gold-silicon films that locally initiated a range of stochastic non-equilibrium thermo- and hydrodynamic relaxation processes. Such a single-step, high-throughput fabrication technique can be easily scaled and seamlessly integrated into existing manufacturing processes ..."

Comment 3. The discussion regarding the quantum efficiency (QE) of Au/Si nanostructures appears somewhat unclear. While the field enhancement factor is linked to the S-to-V value of the Au/Si particles, and the silicon grain size is fitted according to the KAMJ model, the resulting implications regarding the increase in the amount of amorphous silicon in determining QE are conflated. It would be beneficial to reorganize this section for better clarity and comprehension.

Our reply.

We thank the Reviewer for raising this question. In the section “*Inner structure and multi-resonant nature of Au/Si particles*”, we attempted to summarize a large number of interesting results and reflections in a concise manner, but in doing so, we, indeed, lost some of the quality of our narrative.

There are *four* main results in this section that we particularly wanted to highlight for a Reader:

1) *The internal arrangement of our particles is formed stochastically and cannot be predetermined by any existing technology.* This thesis is supported by our general description of the random processes underlying the particle formation, as well as by our estimation of durations of grain nucleation and growth, which we obtained using the KAMJ model. Thus, *the second paragraph* of the section is devoted to the description of this result. In order to save space in the main body of the article, we wrote the part with a detailed description of all stages of Au/Si melt cooling in the Supplementary Note 4.

2) *The comparatively high QE values of our Au/Si particles originate from the high density of hot-spot modes supported by their internal gold network.* Indeed, as we showed in our numerical simulations, these plasmon excitations enable strong field localization within silicon grains in a broad spectral range, which directly affects the recombination rates of hot carriers and, ultimately, enhances the system's QE. *The third paragraph* of the section is devoted to the description of this result.

3) *The greater the S-to-V value of the Au network of the Au/Si particle, the more effectively the field is confined in its silicon grains at different wavelengths; hence, the better QE the particle will demonstrate.* To support this idea, we conducted a major investigation that included a series of numerical simulations (Figure 3e) as well as overall analysis and interpretation of the obtained results. Since many of these technical actions performed are not key to understanding the main purpose of the work, we have placed them in the Methods section. *The fourth paragraph* of the section is devoted to the description of this result.

4) *The larger particles, in general, possess the lower QE values.* This hypothesis was confirmed experimentally (Figure 3d) by measuring a QE map of one of the Au/Si microstructures consisting of many hybrid particles. We explained this result by combining the outcomes from the previous three points. Namely, based on the description of the Au/Si melt solidification process (placed in the Supplementary Note 4), we pointed out that the larger particles have, in general, the lower S-to-V value of the Au network. And based on the result from point (3), we were able to argue that lower

S-to-V results in lower QE. *The fifth paragraph* of the section is devoted to the description of this result.

When describing the result (4) in the main text, we also wrote the following sentence: “However, if the droplet size is small enough, the ratio of amorphous silicon increases, weakening the particle's nonlinear properties.” This particular sentence can cause confusion for a Reader. In fact, with this phrase we wanted to draw a Reader's attention to the thermodynamic processes of particle solidification and highlight that the relationship between the S-to-V and the QE of our particles is not that simple. Indeed, the statement from result (4) may lead to false conclusions if the thermodynamics of particle solidification is not taken into account. Specifically, we wanted to emphasize that, in addition to crystallization of silicon, there is also a competing process of amorphization that begins to dominate at high cooling rates (which corresponds to small particle sizes). As a result, for particle sizes smaller than ~300 nanometers (according to our mild estimates), the proportion of amorphous silicon increases, which has a negative effect on the generation of PL. In order to stay in the framework of formatting rules and focus more deeply on the PUF-related sections we have provided a more detailed description of this aspect in the Supplementary Notes 4 and 6 and included a reference to it in the main text.

To make this point clearer for a Reader we have modified one of the section paragraphs (modifications are highlighted in green):

*“Ultimately, it is important to shed light on the following logical chain. Since the cooling rate is inversely proportional to the droplet radius⁴², the larger the size of an Au/Si melt is, the longer it takes to solidify (Supplementary Note 6). Consequently, the characteristic time for Si grain growth increases, allowing small grains to coalesce into larger ones⁵⁷. This, in turn, results in a less developed Au-enriched network with lower S-to-V values. Finally, according to our simulations, this indirectly results in a decline in the particle's QE. ~~However, if the droplet size is small enough, the ratio of amorphous silicon increases, weakening the particle's nonlinear properties.~~ Therefore, there is a certain relationship between the size and QE of the fabricated hybrids, which is consistent with the results of QE mapping: larger particles possess poorer up-conversion characteristics (**Figure 3d**). ~~Nevertheless, it should be noted that the presented arguments make a number of assumptions and do not consider, for example, the formation of amorphous silicon, which becomes dominant with sufficiently small particle sizes and can negatively affect the PL generation (see Supplementary Note 4).~~”*

Comment 4. In the Reviewer's personal assessment, the robustness of the content in the PUF section appears to be weaker compared to the preceding discussion on the development of nanostructure fabrication processes. For instance, the data presented in Figure 4e seems to exhibit forms that are not commonly utilized in conventional PUF research. Fundamentally, an in-depth examination is needed to determine whether the PUF data utilized by the authors is genuinely random. For instance, while the current study extracts a set of five separate parameters from the PL data, it raises questions about whether these parameters can truly be considered distinct. In typical PUF research, a process is followed to verify the uniqueness and randomness of the key obtained, often through tests like the NIST randomness test to ensure that no intrinsic patterns exist. This study appears to lack such robustness. Additionally, the practice of varying polarization while collecting PL data for a single sample may pose similar concerns.

Our reply.

We thank the Reviewer for this important comment. In this work, in addition to a thorough investigation of the physics underlying the formation and optical properties of Au/Si nanoparticles, we have presented three distinct PUF protocols. Due to space constraints, we had to relocate a significant amount of data and technical calculations that would commonly be included in the main body of a typical PUF paper to the Methods or Supplementary Notes. Next, we address each part of this comment step by step.

1) > For instance, the data presented in Figure 4e seems to exhibit forms that are not commonly utilized in conventional PUF research.

(our reply)

Figure 4e corresponds to the second PUF protocol proposed in our work. This protocol is based on the analysis of unique PL images that we obtain under unfocused laser beam excitation of our laser-printed microstructures. The algorithm for using this PUF is similar to that of the first protocol. Specifically, we assume that the PUF manufacturer will compile a database of PL photos of all created labels. To verify a PUF, a comparison will be made between the PL image of the label taken by the user and the one stored in the database.

In this work, we adopted a method for comparing such photos using computer vision algorithms. Similar methods for authenticating unique PUF images have been already proposed in several recent studies [1-7]. This approach, which does not require obtaining binary keys, has several advantages, including fast processing, markerless authentication, and the ability to authenticate complex features [2]. It is also tolerant of variations in illumination, rotation, and magnification conditions.

Our method involves two main steps: first, the program detects the features (or key points) of each of two given images. Then, it compares these features to find similar points that could be the same feature in both photos. The full description of the method, including the names of the algorithms used, can be found in the Methods section. The number of matches found between two photos serves as an indicator according to

which a decision on verification can be made. Indeed, as Figure 4e shows, there is a considerable gap between the number of matches found during intra- and inter-comparison, which justifies the proposed concept. In other words, after conducting about 2000 comparisons, we determined that the number of matches found between photos of different labels turns out to be much less than the matches found between different photos of the same label. These results allow for the determination of a suitable threshold value (for example, 20), ensuring a wide range of authenticity even in images captured under diverse conditions. Notably, the number of features found in each photo was about 500, and the comparatively large width of the interdevice distribution demonstrates the high influence of the variations in the laser excitation conditions on the resulting PL image.

Referring specifically to Figure 4e, we believe that it has a fairly standard form of two Gaussian-like distributions, which is typical for describing the performance of the majority of PUF encoding algorithms. To provide the Reviewer with a better perspective on this matter, we have compiled an image consisting of several similar figures from other PUF-related works (see **Figure R1**).

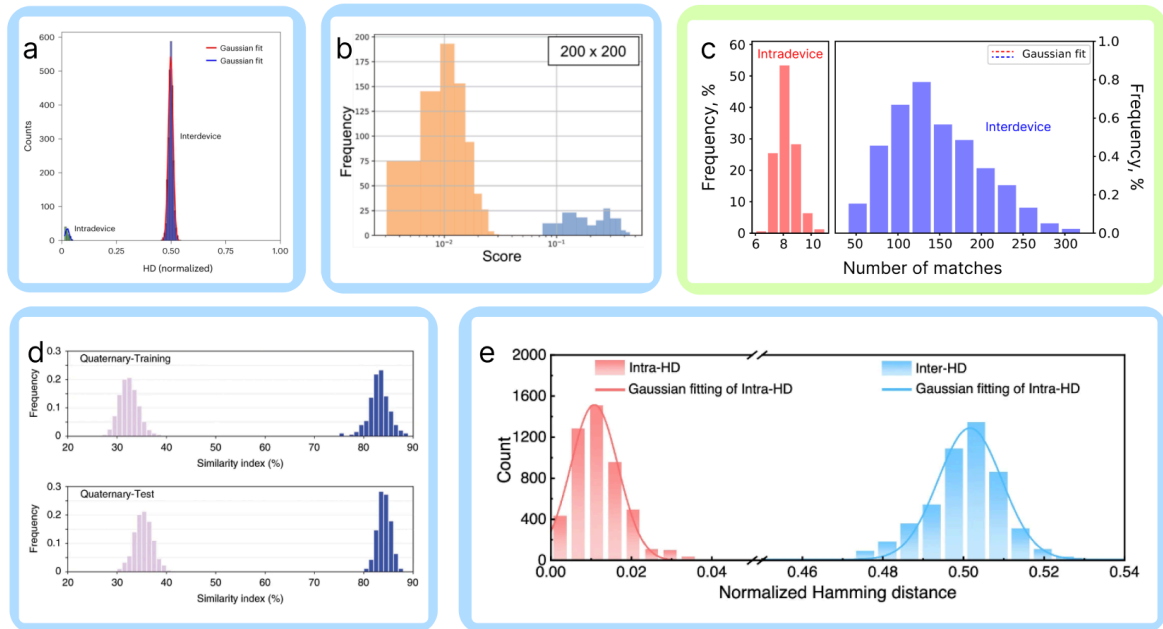


Figure R1. Distribution of the decision metrics for inter- and intra-comparisons of PUFs from different works. (a) Ref [1], (b) Ref [8], (c) This work, (d) Ref [9], (e) Ref [10]

The main difference between the presented figures lies in the metric used to make validation decisions. While in our work we used the number of matches found between two images, in Refs [1, 10] the authors used the normalized hamming distance, in Ref [9] – similarity index, in Ref [8] – match score. However, it is important to mention that the relation between all of these metrics is very straightforward:

$$\begin{aligned} \text{"Similarity index between 2 images"} &= \text{"Number of matches between them"} / \text{"The total number of features found"} \\ \text{"Hamming Distance"} &= 1 - \text{"Similarity index"} \\ \text{"Match Score"} &= \text{"Similarity index"} \end{aligned}$$

In our work we have chosen to use the Number of matches as the most laconic and understandable metric. We hope that we understood this Reviewer's comment correctly and were able to provide a consistent answer to it.

To make this part of the work more clearer for a Reader, we added additional references to works with computer vision-enabled authentication (Refs [1] and [7]) and modified several sentences in the main body of the work and the Methods section. We have also calculated an encoding capacity for this authentication method using the model established by Carro-Temboury et al [11]. The obtained value is 10^{141} , and our calculations are presented in Supplementary Note 8.

Please, see the paragraph from the main text with our modifications highlighted in green color:

"The second authentication concept is based on direct PL imaging using a digital camera with a standard 10x objective, in which an unfocused laser beam illuminates the whole label area at once (Methods). We revealed that photos captured this way display an unrepeatable spatial distribution of PL intensity for any of the laser-printed patterns. This is due to the large influence of microscale hydrodynamic instabilities associated with Au/Si microstructures' creation. Thus, such PL images can be successfully used as unclonable keys. To prove this, we printed a number of visually identical Yin-Yang symbols and collected a database of their PL photos, each time changing the focus accuracy and shifting the position of the center of the pump laser beam. To correctly validate the obtained pictures, we developed an algorithm based on computer-vision techniques (see Methods for more information). In short, when comparing two images, the number of their matches is calculated by analyzing the brightest areas (Figure 4d). Figure 4e shows the distribution of the number of matches obtained during intra- and inter-comparison of 60 captured images. ~~There is a considerable gap between these two sets of values, which justifies the proposed concept.~~ There is a considerable gap between these two sets of values, which allow us to determine a suitable threshold value, ensuring a wide range of accuracy, even for images captured in diverse conditions. Furthermore, the encoding capacity of this PUF model is estimated to be about 10^{141} (Supplementary Note 8 and Supplementary Fig. 16). However, this method is based mostly on microscale spatial randomness, using only PL intensity. Therefore, to fully realize the potential of our PUFs, we should encode their PL spectra individually, taking into account every piece of spectral information."

References from the answer:

- [1] Zhang, Junfang, et al. "An all-in-one nanoprinting approach for the synthesis of a nanofilm library for unclonable anti-counterfeiting applications." *Nature Nanotechnology* 18.9 (2023): 1027-1035.
- [2] a) Esidir, Abidin, et al. "Food-grade physically unclonable functions." *ACS applied materials & interfaces* 15.35 (2023): 41373-41384. b) Esidir, Abidin, et al. "Unclonable features via electrospraying of bulk polymers." *ACS Applied Polymer Materials* 4.8 (2022): 5952-5964. c) Esidir, Abidin, et al. "Ultradurable Embedded Physically Unclonable Functions." *ACS applied materials & interfaces* 16.13 (2024): 16532-16543.
- [3] Sakir, Menekse, et al. "Silver nanoflowers with SERS activity and unclonable morphology." *Materials Today Chemistry* 29 (2023): 101423.
- [4] Kustov, Pavel, et al. "Mie-Resonant Silicon Nanoparticles for Physically Unclonable Anti-Counterfeiting Labels." *ACS Applied Nano Materials* 5.8 (2022): 10548-10559.
- [5] Lee, Sangsun, et al. "Graphene-based physically unclonable functions with dual source of randomness." *ACS applied materials & interfaces* 15.28 (2023): 33878-33889.
- [6] Kiremitler, N. Burak, et al. "Tattoo-Like Multi-Color Physically Unclonable Functions." *Advanced Optical Materials* 12.12 (2024): 2302464.
- [7] Han, Fei, et al. "Self-assembly of coordination polymers on plasmonic surfaces for computer vision decodable, unclonable and colorful security labels." *Journal of Materials Chemistry C* 7.42 (2019): 13040-13046.
- [8] Arppe-Tabbara, Riikka, Mohammad Tabbara, and Thomas Just Sørensen. "Versatile and validated optical authentication system based on physical unclonable functions." *ACS applied materials & interfaces* 11.6 (2019): 6475-6482.

- [9] Gu, Yuqing, et al. "Gap-enhanced Raman tags for physically unclonable anticounterfeiting labels." *Nature communications* 11.1 (2020): 516.
- [10] Wang, Kun, et al. "All-silicon multidimensionally-encoded optical physical unclonable functions for integrated circuit anti-counterfeiting." *Nature Communications* 15.1 (2024): 3203.
- [11] Carro-Temboury, Miguel R., et al. "An optical authentication system based on imaging of excitation-selected lanthanide luminescence." *Science advances* 4.1 (2018): e1701384.

2) > Fundamentally, an in-depth examination is needed to determine whether the PUF data utilized by the authors is genuinely random. For instance, while the current study extracts a set of five separate parameters from the PL data, it raises questions about whether these parameters can truly be considered distinct. In typical PUF research, a process is followed to verify the uniqueness and randomness of the key obtained, often through tests like the NIST randomness test to ensure that no intrinsic patterns exist. This study appears to lack such robustness.

(our reply)

We thank the Reviewer for this extremely important comment. Indeed, the statistical characterization of the generated unclonable keys is one of the most essential and common parts in any PUF research. In our work, we proposed three different PUF encoding protocols, ranging from the most basic ones (first two models of PUF security labels) to more advanced and beneficial (the last, third PUF-based OTP concept). Below, we examine the randomness for each of the three presented types of PUFs. In short, our first two PUF protocols suffer from intra-correlations within unclonable keys, which reduces their degree of randomness (nevertheless, we take this fact into account when evaluating PUF performance), while our third, most innovative approach successfully passes NIST tests and demonstrates great entropy values.

a) Our first PUF protocol is based on PL mapping and decomposition of the measured maps into the set of five, each corresponding to a specific PL feature (with its own physical origin). Like the Reviewer suggested, we studied the possibility of correlations between different PL parameters used to encode our PL maps. After a series of investigations, we have acknowledged that, despite the distinct physical origin of the retrieved set of features, there is a minor correlation between them. Also, due to the uneven filling of pixels (structures) in the QR code, some non-random relations are manifested when comparing different maps of the same feature. Such correlations reduce the total number of degrees of freedom of our PUF label and, consequently, its true encoding capacity. And, as it turns out, they also lead to unsatisfactory results in NIST randomness tests.

Nevertheless, it is important to note that NIST tests are specifically designed to validate only the absolute randomness of samples. In practical applications, keys with lower entropy can still offer effective protection against counterfeiting. In this case, however, it is crucial to correctly assess the extent to which the presence of non-random patterns reduces the degree of randomness of these keys.

In order to address this matter, we considered the notion of an Effective Sample Size (ESS)[1]. This metric estimates the number of independent draws that carry the same amount of unique information as a given sample. If the sample is truly random, its ESS is close to its actual size; however, the presence of correlations within the sample reduces its ESS. It can be argued that the estimation of ESS may be used as an

alternative to NIST tests in the case of correlated data. We have calculated ESS of our samples according to the following formula[2]:

$$ESS = \frac{M \cdot L}{1 + 2 \sum_{t=0}^{2m+1} \rho(t)},$$

where M - the number of chains (keys) in a sample, L - their length, $\rho(t)$ - estimates of autocorrelation at lag t , m - the largest integer such that $\rho(2m) + \rho(2m+1)$ is still positive. Considering samples of five keys (total size $N = M \cdot L = 5 \cdot 100 = 500$), their effective sizes were calculated, taking into account auto-correlations within each key as well as correlations between different keys. As a result, the mean ESS value (after a series of calculations) of approximately 173 was obtained. Therefore, the true encoding capacity can be estimated as $EC = k^{ESS \cdot (1-\beta)} \simeq 10^{54}$ (where $k=5$ is the number of clusters prescribed during the clusterization process, $\beta=0.55$ is the threshold value of the Hamming distance) instead of $k^{500 \cdot (1-\beta)} \simeq 10^{157}$.

Ultimately, we acknowledged the existence of correlations in the obtained PUF keys, but we showed that this is not a big problem and only leads to a decrease in the final encoding capacity (from 10^{157} down to 10^{54}). As a result, the proposed encoding method can still be successfully used for PUF-related industrial applications.

In order to draw a Reader's attention to this point, we have modified the corresponding paragraph from the main text:

*"... The label is considered genuine if the Hamming Distance (HD) calculated for all five keys does not exceed a specified number (0.55, see Supplementary Note 7). **Figure 4c** demonstrates a pairwise matching map characterizing our method's performance based on the analysis of 15 different QR codes. The values in the five 15x15 blocks located on the diagonal of this map show the HD between the keys corresponding to the same PL characteristic, while other blocks mark the ~~correlation~~ relation between vectors of different features. It is important to acknowledge that, despite the distinct physical origins of the five selected PL features, there exists a slight correlation among them. Additionally, the uneven distribution of pixels (structures) within the QR code results in observable non-random relationships when comparing different maps of the same feature. These correlations ultimately diminish the overall degrees of freedom in our PUF label, thereby reducing its true encoding capacity. Taking into account these inevitable but acceptable correlations and the HD gates set for authentication, we assessed the number of all the possible unique PUF labels distinguishable by our validation algorithm: $\sim 10^{54}$ (more info can be found in **Methods**). This value is enough for the successful use of the label¹; if necessary, it can be boosted by increasing the mapping resolution."*

b) Our second PUF protocol is based on the unique intensity distributions observed in PL images captured with a standard digital camera under unfocused laser beam excitation. In the main body of the manuscript, we tried to explain the physical origins of the distinctive intensity distributions seen in each of the captured PL images. First, during fs-laser printing of our hybrid microstructures, hydrodynamic instabilities arise from ultrafast heating and subsequent melt perturbations [3], leading to the formation of randomly located Au/Si particles. Additionally, the internal organization of each particle,

which, as we described in detail, greatly influences its PL intensity, is significantly affected by stochastic processes underlying the solidification of the Au/Si melt. These factors contribute to our statement that each observed PL image has a random component.

However, of course, it is important to acknowledge that each PL image also contains significant predetermined background information, which effectively reduces the overall perception of randomness. For example, when we binarize our images and evaluate the uniformity and uniqueness of the resulting bits, we observe values of 0.13 and 0.17, respectively — well below the ideal value of 0.5. This reduction in randomness is due to the presence of patterns, such as the predetermined Ying-Yang symbol, and the fact that each bright area typically occupies several bits or more. Additionally, the density of particles exhibiting bright PL responses is considerably lower than what would be required in optimal situations. Generally, these issues are common in PUFs based on image analysis, which take advantage from both conventional security labeling approaches and the PUF concept [4-7]. Despite these challenges, we were able to calculate the encoding capacity of our PUF using a well-established model that accounts for these problems (see Ref [4]).

Finally, we would like to note that the key advantage of this PUF protocol is its relatively fast acquisition time (approximately 10 seconds for an entire image) along with a straightforward readout process. However, in terms of generating high-quality unclonable keys and providing robust protection, our next, third PUF protocol proves to be the most innovative and advantageous.

c) In accordance with the Reviewer's advice, for our third PUF protocol (which is based on ML-driven encoding of individual PL spectra) we have successfully implemented NIST testing. For this, we randomly selected 400 distinct embedding keys from our database and subjected them to a series of randomness tests from the NIST test suite. It is important to note that, due to the continuous distribution of our key values (Supplementary Fig. 21), we binarized them by comparing each embedding coordinate's value to its average. The results of these tests are presented in **Table R1**.

NIST statistical test	Average Score	Pass percentage
Monobit	0.638	100%
Frequency Within Block	0.273	98.5%
Runs	0.493	99.5%
Longest run	0.252	92.8%
Discrete Fourier Transform	0.444	97.2%
Non Overlapping Template Matching	0.762	95.2%
Serial	0.504	99.5%
Approximate entropy	0.438	97.8%
Cumulative sums	0.526	100%

Table R1. Summary of the randomness tests of binary sequences retrieved from the ML-generated embeddings of unique PL spectra

Additionally, we calculated the information entropy of our keys, which revealed a high degree of unique information saturation, as well as complete uniformity and unpredictability in the obtained embeddings (see Supplementary Note 14 and Supplementary Fig. 20).

To provide a Reader with this new and valuable information, we created Supplementary Note 13 (“NIST testing of ML-generated embeddings”), Supplementary Note 14 (“Calculating information entropy of ML-generated embeddings”), Supplementary Figure 20 (“Results of the calculation of entropy distributions per each embedding dimension”), Supplementary Table 2 (“Summary of the randomness tests of binary sequences retrieved from the ML-generated embeddings of unique PL spectra”) and added the following sentences to the main body of the manuscript:

“To ensure the uniqueness and randomness of the generated embedding keys, we evaluated them using the NIST randomness test suite⁶², yielding positive results (Supplementary Note 13 and Supplementary Table 2). Furthermore, the computed information entropy values for each embedding coordinate indicate a high degree of unique information saturation, along with complete uniformity and unpredictability of the obtained keys (Supplementary Note 14 and Supplementary Fig. 20)”

References from the answer:

- [1] Vehtari, Aki, et al. "Rank-normalization, folding, and localization: An improved $\hat{R}$ for assessing convergence of MCMC (with discussion)." *Bayesian analysis* 16.2 (2021): 667-718.
- [2] Kumar, Ravin, et al. "ArviZ a unified library for exploratory analysis of Bayesian models in Python." *Journal of Open Source Software* 4 (2019): 1143.
- [3] Kuchmizhak, Aleksandr, et al. "Hydrodynamic instabilities of thin Au/Pd alloy film induced by tightly focused femtosecond laser pulses." *Applied Surface Science* 337 (2015): 224-229.
- [4] Carro-Temboury, Miguel R., et al. "An optical authentication system based on imaging of excitation-selected lanthanide luminescence." *Science advances* 4.1 (2018): e1701384.
- [5] Sun, Ningfei, et al. "Random fractal-enabled physical unclonable functions with dynamic AI authentication." *Nature Communications* 14.1 (2023): 2185.
- [6] Liu, Yang, et al. "Inkjet-printed unclonable quantum dot fluorescent anti-counterfeiting labels with artificial intelligence authentication." *Nature communications* 10.1 (2019): 2409.
- [7] Liu, Yang, et al. "Unclonable perovskite fluorescent dots with fingerprint pattern for multilevel anticounterfeiting." *ACS applied materials & interfaces* 12.35 (2020): 39649-39656.

3) > Additionally, the practice of varying polarization while collecting PL data for a single sample may pose similar concerns.

(our reply)

We appreciate the Reviewer for highlighting this important point. As we were also concerned about the possible similarity of PL signals measured under different pumping laser polarizations, we presented two arguments that support the viability of our concept.

Firstly, existing literature (that describes similar sponge-like types of structures) indicates that the unique multi-resonant internal structure of our particles should significantly influence their polarization-dependent optical behavior [1,2]. Indeed, depending on the polarization of the incident laser pump, various plasmonic hot-spot modes can be excited within the particle. This excitation directly impacts the field enhancement spectra in the silicon grains, leading to alterations in the Purcell factor values in the optical range. These alterations will be significant if the difference between incident polarizations is sufficient enough.

Secondly, our experimental results demonstrate that these changes ultimately modify the shape of the measured PL spectra (see Supplementary Figure 18). To quantitatively confirm that the spectra obtained under different pumping polarizations are really distinct, we calculated a pairwise distance heatmap for their ML-generated embeddings

(see **Figure R2**). Recall that in our proposed algorithm for comparing individual spectra, we established a threshold distance value of 41.3, which determines whether the spectra are considered identical or not. The results clearly indicate that spectra measured under different pump polarizations are classified as different by our comparison algorithm.

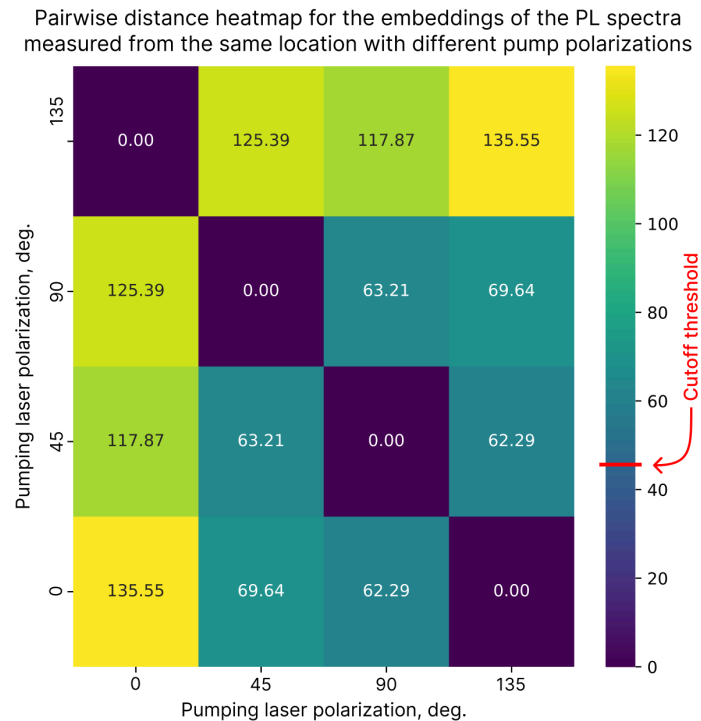


Figure R2. Pairwise distance heatmap for the embeddings of the PL spectra measured from the same location with different pump polarizations.

Furthermore, if we were to increase the number of pumping polarizations—such as using increments of 0, 10, or 20 degrees—we would find that spectra measured under nearly identical polarization excitations exhibit very similar shapes. Therefore, we chose to focus on polarizations with a 45-degree incremental step for our analysis.

As a result, we can use incident laser polarization as an additional parameter to obtain unique PL spectra, each of which will be treated as an individual, unclonable key.

References from the answer:

- [1] Vidal, Cynthia, et al. "Plasmonic horizon in gold nanosponges." *Nano letters* 18.2 (2018): 1269-1273.
- [2] Wang, Dong, and Peter Schaaf. "Plasmonic nanosponges." *Advances in Physics: X* 3.1 (2018): 1456361.

In order to highlight these arguments, we have added Figure R2 to the Supplementary Section 9 as well as the following text:

“Moreover, as we checked on Supplementary Fig. 18, the PL spectra measured under different excitation polarizations are deemed different in our authentication model (since the distance between their embeddings exceeds the cutoff threshold of 41.3), which additionally confirms the viability of the proposed concept.”

Comment 5. In addition, while this study mentions the use of PDMS for encapsulation, additional testing is necessary to determine whether the PUF device can operate effectively under various environmental conditions, such as high temperature, humidity, etc.

Our reply.

We would like to thank the Reviewer for bringing up this important point. Indeed, when considering potential industrial applications, environmental stability of our PUF labels is an essential performance parameter.

We have investigated the stability of our samples under various environmental conditions. To control whether the label response has changed or not, we calculated the distance between embeddings (vectors) generated by our ML model for a pair of spectra measured before and after a certain stability experiment. If the obtained value is lower than the cutoff threshold (< 41.3 , see Supplementary Note 15 or the main body of the manuscript), then our PUFs are stable with respect to the corresponding environmental disturbance.

Time stability:

First, to investigate long-term stability, we have compared the PL spectra of the same Au/Si structures before and after two years of storage under laboratory conditions. These spectra are shown in **Figure R3a**. The distance calculated between the ML-generated embeddings for them is 13.82, which is less than the threshold of 41.3, indicating strong ageing resistance.

Humidity and Sunlight Stability:

We addressed another concern about the stability of our samples in a humid environment or under sunlight exposure, keeping them outside (in open air) for two hours during the daytime in our hometown of St. Petersburg. On the cloudless day of the experiment, the average humidity was 93% and the temperature was around 3°C. As a result, our PUFs performed well, thanks to the exceptional photostability of materials used as well as protective polymer coating (**Figure R3b**).

Continuous laser excitation/measurements:

To confirm the durability of our structures against laser irradiation and to demonstrate the ability of repeatedly measuring their signal, we monitored the stability of PL spectra for a one-hour period of continuous measurements. The **Figure R3c** shows great consistency in the obtained results. The distances corresponding to the measured spectra varied in the range of 7.65-15.06, which is much less than the validation threshold.

Low temperatures:

We also tested the effect of low temperatures on the stability of the PL signal of our hybrid particles. To do this, we stored our samples in a freeze dryer at -19°C for one hour. The PL spectra measured before and after this experiment are shown in **Figure**

R3d. The distance calculated between the ML-generated embeddings for these spectra was 20, which indicates that low temperatures did not affect our PUFs.

Elevated temperature during PL measurements:

It was also important to ensure that temperature variations directly during PL measurements do not affect the resulting spectra. To this end, we heated our PUF labels using a thermoelectric module TB-65-0.6-0.8 with a QJ1803C power supply. We started at room temperature and increased it up to 50°C while simultaneously recording the PL spectra (**Figure R3e**). This experiment also turned out to be successful.

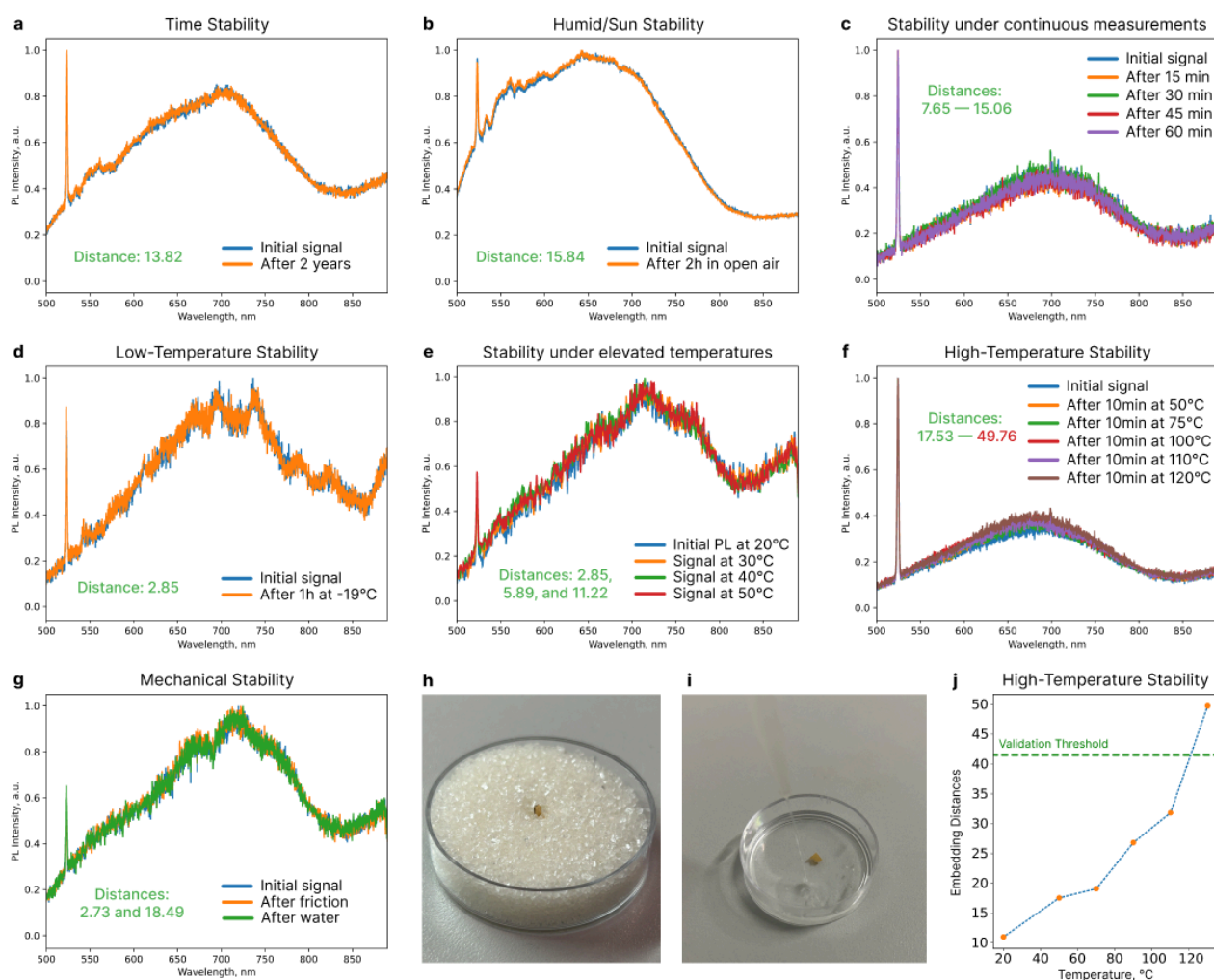


Figure R3. Testing environmental stability of the PL spectra-based PUFs. **(a)** Time stability, **(b)** Humid/Sun stability, **(c)** Stability under continuous laser measurements, **(d)** Low-Temperature Stability, **(e)** Stability under elevated temperatures, **(f)** High-Temperature stability, and **(g)** Mechanical stability were investigated by measuring PL spectra before and after a certain experiment and calculating the distances between them (refer to the Supplementary Note 19). **(h,i)** Photos of mechanical stability experiments, where the sample was exposed to friction with granulated sugar and to the flow of deionized water, respectively (also see Supplementary Movie 1). **(j)** The temperature dependence of the distance calculated between the ML-generated embeddings for the initial and modified (or non-modified) PL spectra during high-temperature stability investigations.

High temperatures:

We also investigated the influence of high temperatures on the PL signal of our Au/Si particles. For this, we heated our samples to temperatures of 50-200°C for 10 minutes using the hotplate function of the MR Hei-Tec setup (Heidolph). The PL spectra measured before and after a heating to a certain temperature are presented in **Figure R3f**. Additionally, **Figure R3j** shows the temperature dependence of the distance calculated between the ML-generated embeddings for the initial and modified (or non-modified) spectra. These results showcase that our samples remain stable under temperatures of as high as ~110°C.

Mechanical abrasion:

To improve the mechanical stability of the created samples, we encapsulated them by spin-coating (1000 rpm, 30 s) polydimethylsiloxane (PDMS). The applied PDMS layer with a thickness of about 300–500 microns had practically no negative effect on the measured PL signal due to its transparency in the visible and near-infrared ranges. We tested the stability of our PDMS-coated samples by subjecting them to various mechanical stresses, such as friction with granulated sugar and flow of deionized water (see **Figure R3h,i** and Supplementary Movie 1). After these tests, we did not observe any changes in the appearance of the sample or in the form of measured PL spectra (**Figure R3g**). Therefore, we concluded that our samples are stable under mechanical abrasion.

To sum up, as we have checked, our samples have demonstrated solid results in terms of environmental stability. While we can't say that we have achieved outperforming temperature or mechanical stability (there are extremely stable PUF concepts proposed in the literature, see [1-3]), we do believe there is great potential for our labels to be used for highly reliable protection of valuable goods or identities.

To make this information available for a Reader we created new Supplementary Note 19 ("On the environmental stability of proposed PL-based PUFs") and Supplementary Fig. 24 ("Testing environmental stability of the PL spectra-based PUFs") as well as added the following comment to the Discussion section of the main text:

"Another important point is the environmental stability of our labels: when encapsulated in a polydimethylsiloxane (PDMS) protective layer, they demonstrate robust performance against a variety of typical external disturbances (see Supplementary Note 19 and Supplementary Figs. 23-24)."

References from the answer:

- [1] Sun, Ningfei, et al. "Random fractal-enabled physical unclonable functions with dynamic AI authentication." *Nature Communications* 14.1 (2023): 2185.
- [2] Zhang, Tongtong, et al. "Multimodal dynamic and unclonable anti-counterfeiting using robust diamond microparticles on heterogeneous substrate." *Nature Communications* 14.1 (2023): 2507.
- [3] Esidir, Abidin, et al. "Ultradurable Embedded Physically Unclonable Functions." *ACS applied materials & interfaces* 16.13 (2024): 16532-16543.

REPLY TO THE SECOND REVIEWER

We want to thank the Reviewer for their careful review and useful comments as well as positive evaluation of our manuscript. The detailed answers to all of their comments are presented below.

Comment 1-1. The fraction of particles (or positions) with bright points appears to be quite low within each unit cell. If the unit cell is pixelated for encoding, the probability between "0" and "1" may not be equal. It is recommended to clarify whether this has been considered in deriving the PUF performance.

Our reply.

We thank the Reviewer for this valuable recommendation.

In our work, we presented three distinct protocols for employing hybrid Au/Si particles as a source of physically unclonable keys.

1) In the first protocol, we employed the PL mapping of laser-printed QR codes, subsequently decomposing the resulting maps into five distinct sets, each corresponding to a specific physical parameter. The mapping resolution was 10x10, while the QR code itself consisted of 29x29 microstructures. Consequently, each point on the map collected the PL signal from a varying number of microstructures (see the visual representation of this process in Supplementary Figure 13, which we added in response to comment 3-2). As a result, all obtained maps had some predefined contribution from the QR code's structure. We addressed this issue in the Methods section by considering the concept of Effective Sample Size (ESS)[1]. In short, ESS estimates the number of independent draws that provide an equivalent amount of unique information as a given sample. In a truly random sample, the ESS closely matches the actual sample size; however, correlations within the sample diminish its ESS. For samples consisting of five keys (with a total size of $N = M \cdot L = 5 \cdot 100 = 500$), we calculated their effective sizes while accounting for auto-correlations within each key and correlations between different keys. Ultimately, after a series of calculations, we obtained a mean ESS value of approximately 173 (which also reflects the inevitable but minor correlations between maps corresponding to different PL features). This value was next used when calculating the encoding capacity of this PUF.

2) In the second protocol, we used PL images of laser-printed Yin-Yang drawings that exhibited unique intensity distributions corresponding to the location of the most effective Au/Si particles in terms of PL generation. Though, initially we didn't present the calculation of encoding capacity for this type of PUF, now, thanks to the Reviewers comments, we estimated it using Caro-Temburry's universal model[2] (see Supplementary Note 8). The obtained value was about 10^{67} . Notably, in our calculations,

we took into account the existence of the external Yin-Yang pattern, which, of course, affected the PUF performance.

3) In our third PUF-based protocol for an all-optical OTP token, we utilized individual PL spectra as unclonable PUF keys. According to this protocol, the OTP token represents a sample with a substantial number of laser-printed microstructures. During the enrollment phase of the token, PL spectra are collected from N random positions on the sample, and each spectrum serves as an individual PUF key with an impressive encoding capacity of 10^{290} , independent of the acquisition location (see Supplementary Note 15). To facilitate the precise positioning for PL measurement, we proposed dividing each microstructure into a 5x5 grid (see Supplementary Note 9 and Supplementary Fig. 17). At this grid resolution, the minimum area for signal collection achievable with our setup (1x1 μm) corresponds precisely to the size of an individual cell. Nevertheless, as the Reviewer correctly pointed out, the arrangement of Au/Si particles within the microstructure is random and does not align with the grid's cell locations. Consequently, there may be some infrequent cells that have no particles inside and, as a result, yield weak PL signals. Fortunately, the presence of such cells has a minor impact on the performance of the OTP token. If a weak-signal area is randomly selected during enrollment, it can easily be replaced with another location. Moreover, under sufficiently stable fabrication conditions, we anticipate that the fragmentation of the Au/Si bilayer film into hybrid particles will be uniform, resulting in a high density of particles distributed evenly throughout the microstructure (see Supplementary Fig. 2). Therefore, the occurrence of weak-signal cells will be relatively rare.

References from the answer:

- [1] Vehtari, Aki, et al. "Rank-normalization, folding, and localization: An improved $\hat{R}$ for assessing convergence of MCMC (with discussion)." *Bayesian analysis* 16.2 (2021): 667-718.
- [2] Carro-Temboury, Miguel R., et al. "An optical authentication system based on imaging of excitation-selected lanthanide luminescence." *Science advances* 4.1 (2018): e1701384.

To make these points more clearer for a Reader, we introduced the following modifications in the manuscript text:

1) For the first PUF protocol, in the main text:

"It is important to acknowledge that, despite the distinct physical origins of the five selected PL features, there exists a slight correlation among them. Additionally, the uneven distribution of pixels (structures) within the QR code results in observable non-random relationships when comparing different maps of the same feature. These correlations ultimately diminish the overall degrees of freedom in our PUF label, thereby reducing its true encoding capacity. Taking into account these inevitable but acceptable correlations and the HD gates set for authentication, we assessed the number of all the possible unique PUF labels distinguishable by our validation algorithm: $\sim 10^{54}$ (Methods). This value is enough for the successful use of the label¹; if necessary, it can be boosted by increasing the mapping resolution."

2) For the second PUF protocol, see the newly added Supplementary Note 8 and Supplementary Fig. 16. Also, we added this sentence in the main text:

"Furthermore, the encoding capacity of this PUF model is estimated to be about 10^{141} (Supplementary Note 8 and Supplementary Fig. 16)."

3) For the third protocol, the following text was added to the Supplementary Note 9.

“It should be noted, though, that the arrangement of Au/Si particles within the microstructure is random and does not align with the grid's cell locations. Consequently, there may be some infrequent cells that have no particles inside and, as a result, yield weak PL signals. Fortunately, the presence of such cells will have a minor impact on the performance of the OTP token. If a weak-signal area is randomly selected during enrollment, it can be easily replaced with another location. Moreover, under sufficiently stable fabrication conditions, we anticipate that the fragmentation of the Au/Si bilayer film into hybrid particles will be uniform, resulting in a high density of particles distributed evenly throughout the microstructure (see Supplementary Fig. 2). Therefore, the occurrence of weak-signal cells will be relatively rare.”

Comment 1-2. A more detailed explanation of the quantitative criteria used for extracting and encoding from collected signals is required. This includes the handling of variations in PL intensity of individual nanoparticles and the pixelation process for circular PL images from different positions.

Our reply.

We thank the Reviewer for this comment. Below, we provide a detailed overview of the mathematical procedures employed to extract the digitized keys for each of the three proposed PUF-based concepts.

In our first PUF protocol (PL mapping + spectra decomposition), we encoded 10×10 PL maps (i.e., arrays of a total of 100 PL spectra) measured from different laser-printed QR codes. These maps were decomposed into five distinct maps, each representing a specific PL feature and consisting of 100 quantitative values. The mathematical formulas utilized for this process can be found in the Methods section. Subsequently, we applied a clustering procedure (Jenks optimization method with the number of clusters set to 5) to each map, converting them into arrays of numbers ranging from 0 to 4. Finally, these 10x10 arrays were stored as 100-dimensional keys through a left-to-right, line-by-line reading approach.

For our second PUF protocol, we used PL images of circular Ying-Yang symbols. For this, the images were resized to 500x500 pixels, followed by the application of a Gaussian blurring procedure using a 5x5 kernel. The processed images were then stored in the database, and their authentication was performed directly using computer vision algorithms (further details can be found in the Methods section).

In our third PUF-based protocol, we encoded individual PL spectra with a trained machine learning model. The input data for the model comprised the 2048-dimensional PL spectrum (in the range from 500 to 900 nm) along with its calculated features, including Fourier and logarithmic transformations, full width at half maximum, full width at quarter maximum, and full width at three-quarters maximum. This resulted in a total input dimension of 6150 (for more information, please refer to the Methods section).

To enhance clarity and facilitate navigation for a Reader, we improved the clarity of the corresponding sections in the main text as well as included relevant links (to the Methods and Supplementary Notes/Figures) throughout the main text.

We have also highlighted the most important information in the newly added Supplementary Figure 13 (“A scheme summarizing the Challenge, Response, Post-processing, Key, and Validation method for the three proposed PUF protocols”), where we graphically present all challenge-response schemes in accordance with Reviewer comment 3-2.

Comment 1-3. Quantifying the unpredictability of the proposed PUF, including calculating information entropy, would provide essential support for the work.

Our reply.

We thank the Reviewer for this valuable comment. According to the Reviewer's advice, we calculated the information entropy for our most advanced and novel PUF, which employs ML encoding of individual spectra. According to the proposed protocol, our trained ML model transforms an input spectra to a 1024-dimensional embedding vector that serves as a unique unclonable key. As demonstrated in Supplementary Figure 21, the coordinates of these vectors are continuously distributed and exhibit a Gaussian-like bell shape.

Therefore, we computed the continuous entropy (or differential entropy) for each of the 1024 embedding dimensions using a database of 2148 different embeddings. Our results are presented in **Figure R4**. The mean value of entropy, which is carried by each embedding coordinate, is approximately 7.3 (with a variance of around 4.3), indicating a very high level of unique information saturation.

Additionally, we presented the results of a more conventional discrete entropy calculation. For this, we binarized the embedding coordinate values based on their deviation from the mean value for each specific coordinate. The mean entropy value obtained is 0.97, with a variance of 0.0009, which implies a uniform level of bit complexity and their complete unpredictability.

We also successfully implemented NIST testing for the binary sequences retrieved from our ML-generated embeddings, which validates their randomness once again (see Supplementary Note 13 and Supplementary Table 2).

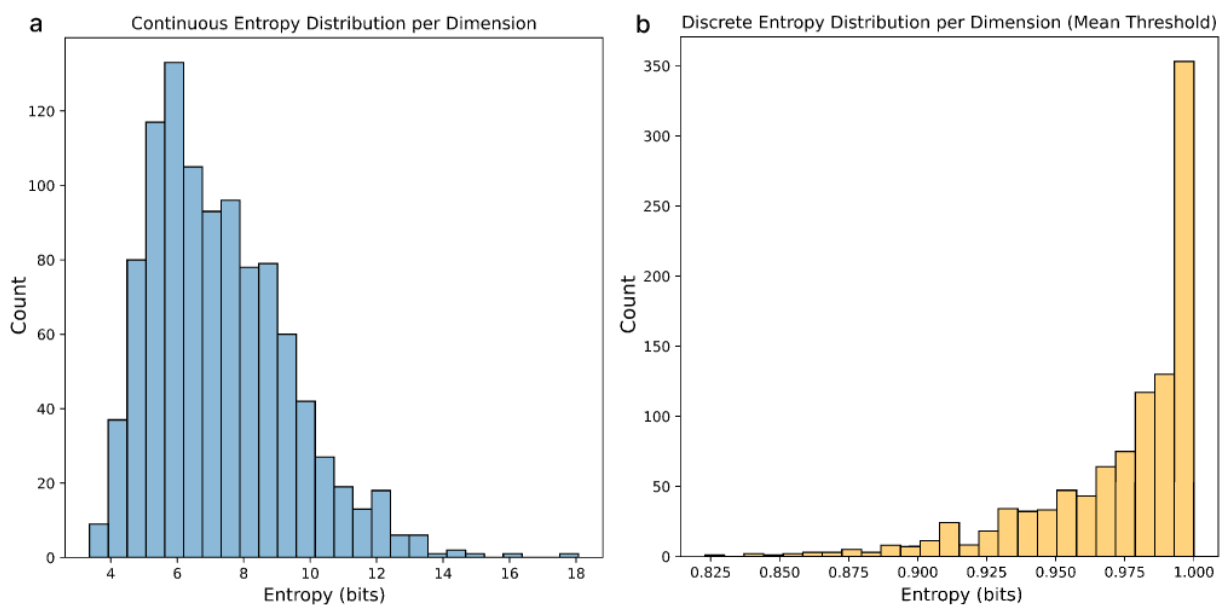


Figure R4. Results of the calculation of continuous and discrete entropy distributions per each embedding dimension.

In order to provide this information for a Reader, we added new Supplementary Note 14 (“Calculating information entropy of ML-generated embeddings”) and Supplementary Fig. 20 (“Results of the calculation of entropy distributions per each embedding dimension”) with the presented results as well as the following sentence in the main body of the manuscript:

“To ensure the uniqueness and randomness of the generated embedding keys, we evaluated them using the NIST randomness test suite⁶², yielding positive results (Supplementary Note 13 and Supplementary Table 2). Furthermore, the computed information entropy values for each embedding coordinate indicate a high degree of unique information saturation, along with complete uniformity and unpredictability of the obtained keys (Supplementary Note 14 and Supplementary Fig. 20)”

[Comment 1-4](#). Presenting a comparative list that indicates the performance level of the proposed PUF, such as the suggested $\sim 10^{54}$ of possible unique PUF labels and $\sim 10^{280}$ of encoding capacity, against other optical PUFs is recommended.

Our reply.

We thank the Reviewer for this valuable suggestion. We have compiled a supplementary table that characterizes the performance of several recent optical PUFs in terms of critical and overall PUF size, storage density, encoding capacity, and acquisition time for a single optical measurement. Please, see Supplementary Table 3. Additionally, we have included our analysis comparing the performance of the proposed PUFs with existing ones, along with a reference to this table in the first paragraph of the Discussion section of the manuscript.

Comment 2-1. Despite the absolute QE values (~1–3.5%) being presented, the QE range for each particle appears narrow. Providing insight into whether these can be distinguished within a meaningful resolution would strengthen the methodology.

Our reply.

We thank the Reviewer for this important comment.

In general, measuring the quantum efficiency of hybrid Au/Si particles is a challenging task due to the uncertainty in the cross section of multiphoton absorption in the investigated system. Therefore, the method we used in this study (which we describe in detail in the Supplementary Notes 1–3 and Supplementary Figs. 4–7) is very approximate and provides only an estimation of the main order of QE. This is commonplace in many related studies on the development of silicon-based white-light sources [1-3].

In this work, we showed our estimation of QE for two main reasons:

- 1) To quantitatively confirm that fabricated structures exhibit intense PL signals, which can be easily measured under comparatively low laser excitation fluences (without damaging the sample), with short acquisition times, and without the need for specialized ultra-sensitive equipment (In addition to the last of the listed, see our answer to the comment 3-6).
- 2) To conduct the QE efficiency mapping and analyze the qualitative relationship between the size and QE of fabricated Au/Si particles. (Since the main sources of error in QE estimation originate from the calculation of total photon losses in the measurement setup, as well as the assessment of the directivity of PL radiation, it can be argued that the relative QE values presented on a single map can be compared with one another with a sufficient degree of reliability.)

To sum up, in the main version of the text, the “~1–3.5%” range was presented mainly to indicate the obtained order of QE values.

To highlight this point, we modified the corresponding sentence as following:

“The obtained efficiencies (on the order of ~1–3.5%) are relatively high for silicon-based PL sources (Supplementary Table 1).”

References from the answer:

- [1] Zhang, Chengyun, et al. "Lighting up silicon nanoparticles with Mie resonances." *Nature Communications* 9.1 (2018): 2964.
- [2] Xiang, Jin, et al. "Crystalline silicon white light sources driven by optical resonances." *Nano Letters* 21.6 (2021): 2397-2405.
- [3] He, Xiaobing, et al. "Si/Au hybrid nanoparticles with highly efficient nonlinear optical emission: implication for nanoscale white light sources." *ACS Applied Nano Materials* 5.8 (2022): 10676-10685.

Comment 2-2. The fabricated structure appears vulnerable to abrasion, especially considering the heavy reliance of the proposed authentication approach on information from individual particles. Presenting the stability of the proposed PUF under conditions such as wear and exposure to environmental factors would address this concern.

Our reply.

We thank the Reviewer for raising this important concern. Indeed, when considering potential industrial applications, environmental stability of our PUF labels is an essential performance parameter.

We have investigated the stability of our samples under various environmental conditions. To control whether the label response has changed or not, we calculated the distance between embeddings (vectors) generated by our ML model for a pair of spectra measured before and after a certain stability experiment. If the obtained value is lower than the cutoff threshold (< 41.3 , see Supplementary Note 15 or the main body of the manuscript), then our PUFs are stable with respect to the corresponding environmental disturbance.

Time stability:

First, to investigate long-term stability, we have compared the PL spectra of the same Au/Si structures before and after two years of storage under laboratory conditions. These spectra are shown in **Figure R5a**. The distance calculated between the ML-generated embeddings for them is 13.82, which is less than the threshold of 41.3, indicating strong ageing resistance.

Humidity and Sunlight Stability:

We addressed another concern about the stability of our samples in a humid environment or under sunlight exposure, keeping them outside (in open air) for two hours during the daytime in our hometown of St. Petersburg. On the cloudless day of the experiment, the average humidity was 93% and the temperature was around 3°C. As a result, our PUFs performed well, thanks to the exceptional photostability of materials used as well as protective polymer coating (**Figure R5b**).

Continuous laser excitation/measurements:

To confirm the durability of our structures against laser irradiation and to demonstrate the ability of repeatedly measuring their signal, we monitored the stability of PL spectra for a one-hour period of continuous measurements. The **Figure R5c** shows great consistency in the obtained results. The distances corresponding to the measured spectra varied in the range of 7.65-15.06, which is much less than the validation threshold.

Low temperatures:

We also tested the effect of low temperatures on the stability of the PL signal of our hybrid particles. To do this, we stored our samples in a freeze dryer at -19°C for one hour. The PL spectra measured before and after this experiment are shown in **Figure**

R5d. The distance calculated between the ML-generated embeddings for these spectra was 20, which indicates that low temperatures did not affect our PUFs.

Elevated temperatures during PL measurements:

It was also important to ensure that temperature variations directly during PL measurements do not affect the resulting spectra. To this end, we heated our PUF labels using a thermoelectric module TB-65-0.6-0.8 with a QJ1803C power supply. We started at room temperature and increased it up to 50°C while simultaneously recording the PL spectra (**Figure R5e**). This experiment also turned out to be successful.

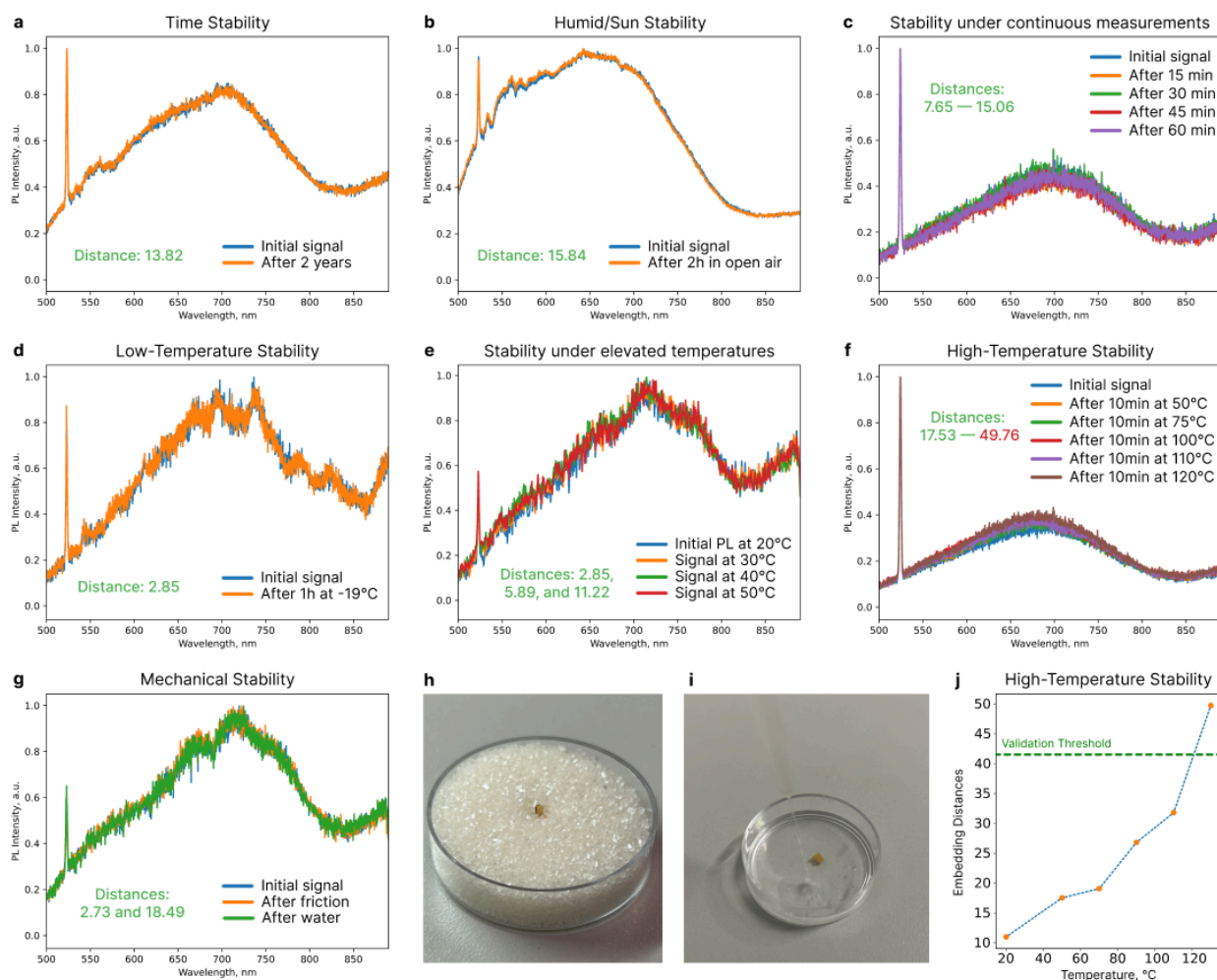


Figure R5. Testing environmental stability of the PL spectra-based PUFs. **(a)** Time stability, **(b)** Humid/Sun stability, **(c)** Stability under continuous laser measurements, **(d)** Low-Temperature Stability, **(e)** Stability under elevated temperatures, **(f)** High-Temperature stability, and **(g)** Mechanical stability were investigated by measuring PL spectra before and after a certain experiment and calculating the distances between them (refer to the Supplementary Note 19). **(h, i)** Photos of mechanical stability experiments, where the sample was exposed to friction with granulated sugar and to the flow of deionized water, respectively (also see Supplementary Movie 1). **(j)** The temperature dependence of the distance calculated between the ML-generated embeddings for the initial and modified (or non-modified) PL spectra during high-temperature stability investigations.

High temperatures:

We also investigated the influence of high temperatures on the PL signal of our Au/Si particles. For this, we heated our samples to temperatures of 50-200°C for 10 minutes using the hotplate function of the MR Hei-Tec setup (Heidolph). The PL spectra measured before and after a heating to a certain temperature are presented in **Figure R5f**. Additionally, **Figure R5j** shows the temperature dependence of the distance calculated between the ML-generated embeddings for the initial and modified (or non-modified) spectra. These results showcase that our samples remain stable under temperatures of as high as ~110°C.

Mechanical abrasion:

To improve the mechanical stability of the created samples, we encapsulated them by spin-coating (1000 rpm, 30 s) polydimethylsiloxane (PDMS). The applied PDMS layer with a thickness of about 300–500 microns had practically no negative effect on the measured PL signal due to its transparency in the visible and near-infrared ranges. We tested the stability of our PDMS-coated samples by subjecting them to various mechanical stresses, such as friction with granulated sugar and flow of deionized water (see **Figure R5h,i** and Supplementary Movie 1). After these tests, we did not observe any changes in the appearance of the sample or in the form of measured PL spectra (**Figure R5g**). Therefore, we concluded that our samples are stable under mechanical abrasion.

To sum up, as we have checked, our samples have demonstrated solid results in terms of environmental stability. While we can't say that we have achieved outperforming temperature or mechanical stability (there are extremely stable PUF concepts proposed in the literature, see [1-3]), we do believe there is great potential for our labels to be used for highly reliable protection of valuable goods or identities.

To make this information available for a Reader we created new Supplementary Note 19 ("On the environmental stability of proposed PL-based PUFs") and Supplementary Fig. 24 ("Testing environmental stability of the PL spectra-based PUFs") as well as added the following comment to the Discussion section of the main text:

"Another important point is the environmental stability of our labels: when encapsulated in a polydimethylsiloxane (PDMS) protective layer, they demonstrate robust performance against a variety of typical external disturbances (see Supplementary Note 19 and Supplementary Figs. 23-24)."

References from the answer:

- [1] Sun, Ningfei, et al. "Random fractal-enabled physical unclonable functions with dynamic AI authentication." *Nature Communications* 14.1 (2023): 2185.
- [2] Zhang, Tongtong, et al. "Multimodal dynamic and unclonable anti-counterfeiting using robust diamond microparticles on heterogeneous substrate." *Nature Communications* 14.1 (2023): 2507.
- [3] Esidir, Abidin, et al. "Ultradurable Embedded Physically Unclonable Functions." *ACS applied materials & interfaces* 16.13 (2024): 16532-16543.

[Comment 3-1](#). On page 3, line 39, the authors emphasize the importance of nanoscale critical dimensions. Supporting this statement with additional references is suggested.

“Nanoscale physical unclonable function labels based on block copolymer self-assembly, *Nature Electronics* 5, 433-442 (2022)”

Our reply.

We thank the Reviewer for this valuable suggestion. The mentioned reference is added to the specified location as [23] Kim, J. H.; Jeon, S.; In, J. H.; Nam, S.; Jin, H. M.; Han, K. H.; Yang, G. G.; Choi, H. J.; Kim, K. M.; Shin, J.; Son, S.-W.; Kwon, S. J.; Kim, B. H.; Kim, S. O. *Nanoscale physical unclonable function labels based on block copolymer self-assembly. Nat. Electron.* 2022, 5, 433–442.

Comment 3-2. Specifying or visually representing the concepts corresponding to Challenge, Key, and Response would aid in comprehension.

Our reply.

We are grateful to the Reviewer for this valuable suggestion. We fully agree that a more complete description of the key generation concept will make understanding of enrollment and authentication process clearer for a Reader. In accordance with the Reviewer's comment, we have added an explanatory image that describes such important steps as Challenge, Response, Pre-processing, Key, and Validation for each of three of the proposed PUF protocols, please, see Supplementary Figure 13. We also added a link to this figure in the main text:

“(see the scheme summarizing the Challenge, Response, Post-processing, Key, and Validation steps for each of these strategies in Supplementary Fig. 13.)”

Comment 3-3. Including brief explanations of newly introduced concepts such as forge-resistance would improve clarity.

Our reply.

We thank the Reviewer for this comment. We have added an explanation of the term forge-resistance to the main text:

“Using only the signal intensity significantly limits forge-resistance (i.e. the ability to withstand attempts at forgery), while relying on purely cryptographic methods loses valuable physical insights embedded within the signal.”

We have also introduced a concept of *storage density of unique information*, which describes the amount of data extracted from a PUF per unit area. A new paragraph, which explains this term and highlights the practical novelty of our work is added to the discussion section:

*“One of the key aspects that distinguishes the presented work is our approach to addressing the structural variations in fabricated Au/Si particles. Since the direct analysis of this internal randomness (with characteristic sizes of 20 nm) requires tedious TEM-based techniques, we proposed using the particles' PL spectra as an alternative, highly capacious source of unclonable keys. In support of this method, we investigated how the multi-resonant nature of our particles establishes a strong linkage between their internal composition and the spectral features of the emitted PL. We have shown that each PL spectrum contains a wealth of unique spectral information, leading to an exceptionally high **storage density** (i.e., the amount of data extracted from a PUF per unit area). Indeed, in our latest protocol, which employs machine learning to encode individual PL spectra, each square micrometer of the label effectively stores 3,720 random bits (Supplementary Note 15). This represents an exceptional storage density that is 2-3 orders of magnitude greater than that of other optical PUFs (see the calculation of this parameter for all of the presented PUF concepts in Supplementary Note 16). Ultimately, the Supplementary Table 3 demonstrates that we have successfully downscaled the characteristic randomness of our PUFs.”*

Comment 3-4. Clarifying whether Weak PUF and Strong PUF are standard terms with quantitative criteria for distinction would provide valuable context.

Our reply.

We thank the Reviewer for this useful comment. The terms “Weak PUF” and “Strong PUF” are well-established and originate from the field of electronic PUFs (see, for instance, Refs [1-7]). While these terms are rather frequent in the literature, there remains some debate regarding the qualitative distinctions between Weak and Strong PUFs [7]. Generally, we align with the definition provided in Ref [1]: *“A weak PUF can only support a small number of challenges (in some cases only a single challenge). A strong PUF can support a large enough number of challenges such that complete determination/measurement of all challenge–response pairs (CRPs) within a limited timeframe is not feasible”*.

Ref [7] made an effort to clarify the criteria for distinguishing between Weak and Strong PUFs. The authors proposed that a Strong PUF should ideally exhibit a number of CRPs that scales exponentially with its size, whereas linear or polynomial growth typically characterizes Weak PUFs. However, this framework has certain limitations, particularly as it applies to electronic PUFs, where response times are sufficiently short—an assumption that may not be true for optical PUFs. Furthermore, it has been suggested that strong PUFs that fit this definition may not actually exist [5, 7].

In our work, we followed the general non-qualitative distinction between Weak and Strong PUFs, while also suggesting that the time required for Strong PUF fabrication should be significantly shorter than the time needed to measure all of its CRPs. Specifically, in the context of our third proposed PUF-based protocol, we estimated this ratio to be approximately 1 to 10^5 (see Supplementary Note 11).

To sum up, while these terms are fairly standard and well-established, the quantitative criteria for their distinction is the subject of long phenomenological discussion. To help Readers who are interested in learning more about this topic, we have included additional references (namely, the Refs 1 and 7 from the answer) in the main text.

References used in the answer:

- [1] Herder, Charles, et al. "Physical unclonable functions and applications: A tutorial." *Proceedings of the IEEE* 102.8 (2014): 1126-1141.
- [2] Ning, Huansheng, et al. "Physical unclonable function: Architectures, applications and challenges for dependable security." *IET Circuits, Devices & Systems* 14.4 (2020): 407-424.
- [3] Che, Wenjie, Fareena Saqib, and Jim Plusquellic. "PUF-based authentication." *2015 IEEE/ACM International Conference on Computer-Aided Design (ICCAD)*. IEEE, 2015.
- [4] Guajardo, Jorge, et al. "FPGA intrinsic PUFs and their use for IP protection." *Cryptographic Hardware and Embedded Systems-CHES 2007: 9th International Workshop, Vienna, Austria, September 10-13, 2007. Proceedings 9*. Springer Berlin Heidelberg, 2007.
- [5] Rührmair, Ulrich, Jan Sölter, and Frank Sehnke. "On the foundations of physical unclonable functions." *Cryptology ePrint Archive* (2009).
- [6] Gao, Yansong, Said F. Al-Sarawi, and Derek Abbott. "Physical unclonable functions." *Nature Electronics* 3.2 (2020): 81-91.
- [7] McGrath, Thomas, et al. "A puf taxonomy." *Applied physics reviews* 6.1 (2019).

Comment 3-5. On page 2, line 34, the manuscript does not clearly address whether the previously identified limitations of optical PUFs are effectively overcome in the proposed research.

Our reply.

We thank the Reviewer for this important comment. In the specified part of the work, we identified the following limitations of optical PUFs:

- 1) “current fabrication techniques for strong optical PUFs are often incompatible with the existing manufacturing lines...”
- 2) “...and/or susceptible to sophisticated machine learning attacks”;
- 3) “most PUF designs rely on microscopic spatial features, which threatens their long-term security”.

To clearly highlight how we managed to overcome the mentioned limitations, we significantly expanded the Discussion section, adding two new paragraphs. The first paragraph argues that one of the key novelties of our work is the successful downscaling of critical PUF sizes down to nanolevel (3rd point addressed). The second paragraph (and a part of the third paragraph) discusses the practical side of the work, considering its potential for industrial use (1st point addressed). Regarding the second point, it is important to note that machine learning attacks are primarily applicable to scattering PUFs, such as those using volumetric scattering media [1, 2] (where the entire system contributes to generating each optical response). In contrast, our system uses a distributed architecture in which individual parts are responsible for *independently* generating different responses, which makes ML attacks useless.

References used in the answer:

- [1] Pappu, Ravikanth, et al. "Physical one-way functions." *Science* 297.5589 (2002): 2026-2030.
- [2] Rührmair, Ulrich, et al. "Optical pufs reloaded." *Cryptology ePrint Archive* (2013).

Below we present a couple of sentences from the Discussion section that directly address the identified problems:

“... Indeed, in our latest protocol, which employs machine learning to encode individual PL spectra, each square micrometer of the label effectively stores 3,720 random bits (Supplementary Note 15). This represents an exceptional storage density that is 2-3 orders of magnitude greater than that of other optical PUFs (see the calculation of this parameter for all of the presented PUF concepts in Supplementary Note 16). Ultimately, the Supplementary Table 3 demonstrates that we have successfully downscaled the characteristic randomness of our PUFs...”

“...To create these particles, we used fs-laser excitation of thin gold-silicon films that locally initiated a range of stochastic non-equilibrium thermo- and hydrodynamic relaxation processes. Such a single-step, high-throughput fabrication technique can be easily scaled and seamlessly integrated into existing manufacturing processes...”

Comment 3-6. Responses used for encoding (e.g., images of bright spots on the nanoscale, decomposed PL signals) seem to require specialized equipment or extended acquisition times. Offering a perspective on these points would be beneficial.

Our reply.

We thank the Reviewer for this insightful comment. In general, the use of PL-based security labels requires covert and forensic identification methods. In such an approach, PL labels are verified with specialized equipment that, while complex and costly and requiring metrological certification, also serves as an additional barrier against individuals attempting to compromise or counterfeit the technology. Below, we provide a detailed description of the equipment and acquisition times used in our experiments for each of the three proposed PUF protocols, as well as present a perspective on possible simplifications in the measurement setup that can be made to facilitate technology industrialization.

- a) In our first PUF protocol, based on PL mapping and spectra decomposition, we used a three-axis piezo-stage (AIST Project) for sample positioning, a 10x/0.26NA objective (Mitutoyo M Plan APO NIR) for signal collection, and a laboratory Horiba LabRam HR spectrometer (see more information in **Methods**). Thanks to the sufficient quantum efficiencies of our particles, acquisition times for their PL measurements are quite short and vary within a range from 0.1 to several seconds (depending on the pumping laser fluence set, see Supplementary Fig. 8). Specifically for PL mapping, we set an acquisition time of 0.2 seconds, which consistently yielded low-noise PL signals.
 - b) In our second PUF protocol, based on direct PL imaging, we used a standard digital Canon 500d camera instead of the spectrometer. The acquisition time needed to obtain the whole PL image was 10 s.
 - c) In our third PUF-based protocol, we used a more expensive 100x/0.7NA objective instead of the one mentioned above. The acquisition time was set to be 3 seconds.
- Finally, for PL excitation, an Yb³⁺ laser system (TeMa, Avesta 281 Project) with a center wavelength of 1050 nm, a pulse duration of 150 fs, and a repetition rate of 80 MHz was used.

To give a Reader insight into standard acquisition times for PUF readouts, we compiled a comparative table (see Supplementary Table 3). Our findings indicate that our PUFs perform competitively against their alternatives. To explore potential simplifications in the readout system, we conducted additional experiments using a standard, less sensitive optical fiber spectrometer (Avantes AvaSpec-2048). As shown in Supplementary Note 18 and Supplementary Fig. 22, this industrial spectrometer delivered robust results, achieving efficient PL spectrum measurements with a 1-second acquisition time (see **Figure R6**). It is important to emphasize, though, that obtaining consistent PL spectra, regardless of the type of spectrometer used, requires careful consideration of the spectrometer's quantum efficiency and other critical parameters, such as spectral resolution. These parameters are typically calibrated and certified for most laboratory and industrial equipment. We also propose considering industrial

fiber-optic femtosecond lasers as a reliable and cost-effective alternative for PL excitation.

In conclusion, while our research utilized some specialized laboratory equipment, we demonstrated that the readout process for our PUFs can also be effectively conducted using more accessible industrial fiber-optic equipment. Furthermore, thanks to the sufficiently high quantum efficiencies of our particles, the acquisition times for PL measurements remain comparatively short, as illustrated in Supplementary Table 3.

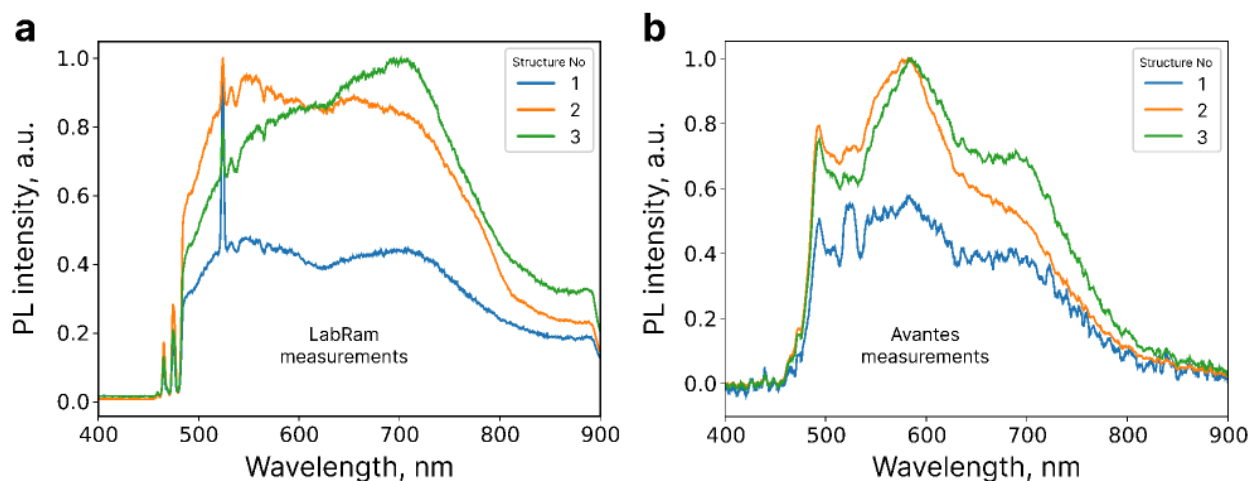


Figure R6. PL spectra measured from different structures with (a) a laboratory Horiba LabRam HR spectrometer and (b) an optic-fiber spectrometer Avantes AvaSpec-2048. In both cases, the acquisition time was 1 second.

To provide this new information for a Reader we modified a Discussion section, adding a new paragraph that consider potential practical applications of our work:

“Considering the potential practical value of our PUFs, it is important to emphasize their key advantage: high-entropy spectral responses controlled by nanoscale structural randomness. This concept provides the highest level of protection, not only in the immediate future but also over many decades to come. This is particularly crucial as we enter an era where traditional PUFs, which rely on microscale spatial randomness, will become increasingly vulnerable due to advancements in precise micro-manipulation techniques. Although in our approach demonstration we have used costly laboratory equipment, the long-term implementation will substantially reduce expenses for each individual PUF label (see Supplementary Note 17 for our cost estimations). Additionally, the rapid advancements in industrial fiber-optic fs-lasers and spectrometers are expected to further enhance the viability of our technology (for example, in Supplementary Note 18 and Supplementary Fig. 22 we showed that our PL measurement setup can be greatly simplified by employing a low-cost commercial spectrometer). Another important point is the environmental stability of our labels; when encapsulated in a polydimethylsiloxane (PDMS) protective layer, they demonstrate robust performance against a variety of typical external disturbances (see Supplementary Note 19 and Supplementary Figs. 23-24). With all of the above, we believe that our approach is going to find its industrial niche in the future.”

Comment 3-7. Describing the advantages of using an optical-based authentication method for OTP verification tokens would add depth to the discussion.

Our reply.

We thank the Reviewer for this valuable comment. In general, any One-Time Password (OTP) verification token should embody a system that securely stores (or unpredictably generates) a substantial number of genuinely random keys. These keys must remain confidential until used, never be reused, and be completely independent of one another [1]. Additionally, in order to ensure perfect protection, it is necessary to ensure that it is almost impossible to gain full access to all the keys stored in the token (as we described in the main body of our work). While such OTP systems have been widely recognized in industry, their practical electronic implementations face a number of limitations in modern cryptographic applications [1-3]. The primary challenge limiting the widespread adoption of OTP schemes lies in the potential vulnerability of electronic hardware to physical attacks, such as discrete reset [4], imaging [5], and freezing [6] techniques, which can compromise partial or complete verification keys. Additionally, it is necessary to provide the generation and secure storage of a huge number of truly random and uncorrelated keys. Therefore, there is a growing quest for novel implementations of the OTP concept, for example, using optical methods [1-3].

At this standpoint, the all-optical OTP verification token proposed in our work offers several notable advantages. First, the optical readout method employed enables the acquisition of high-entropy keys that are stored on the nanoscale with remarkably high storage density. Second, as we demonstrated in the Supplementary Note 12 and Supplementary Fig. 19, the likelihood of a third party being able to randomly access the key required for verification approaches zero, which underscores the confidentiality of the proposed scheme. Finally, our model holds significant promise for the future cryptographic implementations in the upcoming era of photonic computing and optical communications [7-9].

To highlight this important point for a Reader, the following sentence was added in the main text:

“Thus, in contrast to electronic alternatives, which are often vulnerable to physical attacks^{11,12}, our all-optical OTP system offers superior performance through the high entropy and enhanced security of stored keys.”

We have also included a Supplementary Note 10 “On the concept of One-Time Password verification” (and referenced it in the main text) where we provide a more detailed explanation of the OTP token concept and outline the advantages of its optical implementation.

References used in the answer:

- [1] Mazzone, Valerio, et al. "Photonics based perfect secrecy cryptography: Toward fully classical implementations." *Applied Physics Letters* 116.26 (2020).
- [2] Horstmeyer, Roarke, et al. "Physical key-protected one-time pad." *Scientific reports* 3.1 (2013): 3543.
- [3] Di Falco, Andrea, et al. "Perfect secrecy cryptography via mixing of chaotic waves in irreversible time-varying silicon chips." *Nature communications* 10.1 (2019): 5827.

- [4] Anderson, Ross, and Markus Kuhn. "Low cost attacks on tamper resistant devices." International Workshop on Security Protocols. Berlin, Heidelberg: Springer Berlin Heidelberg, 1997.
- [5] Skorobogatov, Sergei P., and Ross J. Anderson. "Optical fault induction attacks." Cryptographic Hardware and Embedded Systems-CHES 2002: 4th International Workshop Redwood Shores, CA, USA, August 13–15, 2002 Revised Papers 4. Springer Berlin Heidelberg, 2003.
- [6] Samyde, David, et al. "On a new way to read data from memory." First International IEEE Security in Storage Workshop, 2002. Proceedings.. IEEE, 2002.
- [7] Matoba, Osamu, et al. "Optical techniques for information security." Proceedings of the IEEE 97.6 (2009): 1128-1148.
- [8] Agrell, Erik, et al. "Roadmap of optical communications." Journal of optics 18.6 (2016): 063002.
- [9] Zhang, Fei, et al. "Meta-optics empowered vector visual cryptography for high security and rapid decryption." Nature Communications 14.1 (2023): 1946.

Comment 3-8. Addressing whether PL wavelengths from different particles with the fabricated nanoscale dimensions and structures remain consistent would clarify the reproducibility of the findings.

Our reply.

We thank the Reviewer for this comment.

The bright broadband PL observed in our experiments arises from the radiative transitions of excited electrons from the conduction band to the valence band within the silicon component of our particles. Due to silicon's indirect band gap, these transitions cover a wide energy range of ~ 1.3 to ~ 3.4 eV, which corresponds to a photon wavelength range of approximately 360 to 950 nm [Nano letters 18.1 (2018): 535-539]. Since the possible PL wavelengths of our Au/Si particles are dictated solely by the band structure of Si, this spectral range remains consistent across different particle samples. Nevertheless, due to the operational ranges of the measurement equipment employed as well as relatively low PL intensities at the edges of the specified range, we consistently detect and analyze (encode) only the most intensive PL within a fixed, narrower range of 500 to 900 nm (see, for example, Supplementary Fig. 5. In order to clarify this point, we added these values in the Methods section when describing the PL spectra used for ML-driven OTP verification). The primary variations observed here lie in the shape and relative intensity of the measured spectra and serve as a source for obtaining unclonable keys.

REPLY TO THE THIRD REVIEWER

We want to thank the Reviewer for their careful review and useful comments as well as time spent for evaluation of our manuscript. The detailed answers to all of their comments are presented below.

Comment 1. While the optical PUF shows potential in generating high-entropy responses, its reliance on PL introduces significant challenges for practical implementation. PL-based systems demand precise excitation sources (e.g., specific wavelengths or intensities) and highly sensitive optical detectors to capture the emitted luminescence accurately. This requirement increases both the complexity and cost of deployment, limiting its suitability for large-scale or resource-constrained environments. Although various optical PUFs have emerged recently, real-world applications require simpler and more practical measurement methods. The mere use of complex equipment to achieve PUF functionality does not inherently justify the academic value of the approach.

Our reply.

We are thankful to the Reviewer for raising these important comments. Indeed, when developing an anti-counterfeiting security solution, it is crucial to consider its potential practical applications and the target market for implementation. Below we present our thoughts, which, as we hope, will help to address all the concerns raised by the Reviewer.

First, we would like to provide some general comments on anti-counterfeiting labels that utilize photoluminescence (PL) of nano- and microscale elements. These labels attract more and more attention in the industry due to advancements in material science and fabrication technologies [1,2]. However, their authentication often requires specific excitation wavelengths provided by specialized pumping sources and detection systems that typically involve a spectrometer. This need for complexity can be explained by two main reasons:

(i) In addition to the security label's spatial design (e.g., special images or unique patterns), the characteristics of the probing radiation and the resulting PL response (including the spectral range and relative line intensities) serve as highly reliable protective features, playing a crucial role in enhancing security. Although the equipment required for this type of authentication can be specialized, costly, and require metrological certification, this complexity simultaneously creates an additional barrier for individuals who will attempt to compromise or counterfeit the technology. So, while this increases the cost of the labels and limits their use for lower-priced items, it simultaneously enhances confidence in product authenticity.

(ii) There are target market segments where the use of PL-based anti-counterfeiting labels is justified by the needs of covert and forensic identification. During these identification processes, PL labels are verified using specialized tools. In forensic contexts, this verification typically relies on advanced laboratory equipment, and only a select group of trained technicians are authorized to perform these checks. In such scenarios, the level of protection for valuable goods is of utmost importance. A notable example of successful implementation of such an approach is the infrared imaging (reflection or absorption) of a 100 Euro banknote [3]. This procedure requires specialized equipment that is accessible to bank employees but not to the average user or potential intruder. Additionally, there is a growing number of companies engaged in the development of spectral measuring equipment that can be designed specifically for such anti-counterfeiting tasks [4-6].

Therefore, PL-based anti-counterfeiting labels, in general, while not overt security technologies, possess significant potential for real-world applications. They are likely to occupy distinct market segments based on label costs, product value, and the necessity for complex authentication and multi-level security systems.

Secondly, we would like to expand on the general motivation of our work and application potential of the proposed PL-based PUFs.

The concept of optical PUF labels has successfully emerged for already a decade now as a new-generation security solution. Up to date, a huge breakthrough has been made in this direction, and two sub-directions of development have naturally emerged. The first one is the industrialization of optical PUFs and the development of ready-to-use, cost-effective technologies applicable to current anti-counterfeiting approaches. A special example of the result of the scientific community here is the Puffin-ID company [7], which successfully grows in the industry. The second, more science-intensive direction in the PUF development is the search for more sophisticated and secure sources of randomness, which is motivated due to advancements in precise micro-manipulation technologies (that will be able to compromise or put at high risk conventional microscale spatial-based PUFs in the near future) [8-9]. In our work we were focused more especially on this second direction.

In a nutshell, the key advantage of the PUF approach presented in our study: high-entropy unclonable spectral responses controlled by *nanoscale* structural randomness. This concept provides the highest level of protection, not only in the immediate future but also over many decades to come. We confirmed this statement in the newly added first paragraph of the discussion section, where we compared our PUFs with existing ones in terms of critical sizes and storage density of unique information (Supplementary Note 16 and Supplementary Table 3). We do acknowledge that our proposed solution is a *conceptual* one and *at present Technology Readiness Level (TRL)* does require the use of costly and complex measurement equipment, but we believe that the motivation behind this totally justifies these practical drawbacks.

Indeed, our work is mostly conceptual, since we utilized laboratory equipment and have not yet conducted engineering optimization of the developed system (which will be essential for advancing this work to higher TRLs). Nevertheless, there is significant potential for optimizing the cost and ease-of-use of our PUFs. For instance,

the spectrometer used in our study (Horiba LabRam HR) is designed purely for scientific experiments and costs 200k Euros. Transitioning from a concept to practical applications allows us to employ simpler and more affordable detection systems. To illustrate this, we replaced the Horiba LabRam HR spectrometer with the less sensitive, industrial fiber-optic Avantes AvaSpec-2048 model, which costs less than \$5,000 — 40 times lower. We conducted PL measurement and found that this replacement did not significantly impact the measurement quality (thanks to the sufficient quantum efficiency of Au/Si particles, see Supplementary Note 18 and Supplementary Fig. 22). Additionally, cost reductions can be achieved through optimizing the optical setup and selecting more affordable fiber-optic femtosecond (fs) lasers; prices for them have been steadily decreasing for the last decades and now start at around \$10,000 [10, 11]. As a result, as we estimated in the Supplementary Note 17, the total price of the equipment needed to verify our PUFs could be reduced to \$20,000 (Though, in our experiments the total cost was approximately \$80,000).

Therefore, with all of the above, we believe that our approach is going to find its industrial niche in the future.

Finally, we would like to take this opportunity to highlight the academic value of our work. In addition to successfully developing nanoscale-enabled spectral PUFs that lead the field in critical size and storage density of random information, we have also conducted a comprehensive investigation of the physics underlying the formation of their unique spectral responses. In particular, we considered the thermodynamics involved in the stochastic formation of complex internal structures within our Au/Si particles (and supported these studies by HAADF-STEM and BF-STEM studies), as well as successfully established the relationships between these random structural characteristics and the unique spectral features of the particles' PL (which was backed by our quantum efficiency estimations and laborious numerical simulations). On top of that, we introduced a novel protocol for employing strong PUFs as the foundation for all-optical one-time password verification tokens, paving the way for the onward PUF-enabled integration of optics and high-end cryptography. Our proposed PUF approach is built on detailed interdisciplinary research that combines femtosecond laser fabrication, materials science, hybrid nanophotonics, and information technology. Notably, our findings are of particular interest to the scientific community specializing in the physics of hybrid metal-semiconductor nanophotonic structures.

In accordance with the Reviewers concerns raised in the first and the third (see further) questions, we modified the discussion section of the manuscript (please, see the modifications made further, after our answer on the third question). We also added new supplementary materials, in particular, Supplementary Notes 16-18 ("On the concept and calculation of storage density", "Calculation of the overall cost of a single PUF label", "PL measurements with an industrial optical fiber spectrometer") and Supplementary Figure 22 ("Testing an industrial optical fiber spectrometer for possible PL measurement"), and Supplementary Table 3 ("The performance of several prominent optical PUFs in terms of critical and overall PUF size, storage density, encoding capacity, and acquisition time for a single optical measurement").

References used in the answer:

- [1] Zhang, Jiawei, et al. "Anti-Counterfeiting Application of Persistent Luminescence Materials and Its Research Progress." *Laser & Photonics Reviews* 18.3 (2024): 2300751.
- [2] Yu, Xiaowei, Hongyue Zhang, and Jihong Yu. "Luminescence anti-counterfeiting: from elementary to advanced." *Aggregate* 2.1 (2021): 20-34.
- [3] <https://www.ecb.europa.eu/euro/banknotes/current/security/html/index.en.html>
- [4] For example, <https://www.edinst.com/product/fls1000-photoluminescence-spectrometer/>,
<https://www.edinst.com/resource/forensic-paint-analysis-raman-microscopy/>
- [5] <https://www.peret.it/index.php/products/security-print/fluosp-spectro>
- [6] <https://www.goyalab.com/>
- [7] <https://www.pufin.id/>
- [8] Kim, Jang Hwan, et al. "Nanoscale physical unclonable function labels based on block copolymer self-assembly." *Nature Electronics* 5.7 (2022): 433-442.
- [9] Zhou, Lei-Ming, et al. "Recent progress on optical micro/nanomanipulations: structured forces, structured particles, and synergetic applications." *ACS nano* 16.9 (2022): 13264-13278.
- [10] <https://www.laserlabsource.com/Solid-State-Lasers/fiber-lasers>
- [11] In general, high-tech technologies tend to decrease in cost when they transition from laboratory settings to mass production and broader applications. For example, while fs lasers are now widely utilized in ophthalmology, their initial application faced skepticism due to steep costs; <https://www.healio.com/news/ophthalmology/20120331/steep-initial-costs-associated-with-femtosecond-laser-for-cataract-surgery>

Comment 2. Furthermore, the manuscript lacks sufficient detail on the number of CRPs that can be practically achieved.

Our reply.

We thank the Reviewer for this important comment. In this work, we introduced three distinct PUF encoding protocols designed for anticounterfeiting and one-time password verification purposes. In our initial manuscript submission, we provided calculations regarding the number of challenge-response pairs (CRPs) that can be practically achieved (that is, encoding capacity, EC) of two out of the three proposed concepts. Specifically, we estimated the EC for the first PUF protocol, which is based on photoluminescence (PL) mapping and spectra decomposition, to be approximately 10^{54} (see Methods). For the third PUF protocol, which relies on comparing individual machine learning-processed spectra, we estimated the EC to be around 10^{280} (see Supplementary Note 15). This information was not clearly highlighted in the manuscript, therefore we are thankful to the Reviewer for noticing this point.

Therefore, in accordance to the Reviewers comment, we have made the following enhancements:

- 1) We calculated the encoding capacity for the second PUF protocol, which is based on direct PL imaging of laser-printed drawings, using the well-established Carro-Tembourry model (see Supplementary Note 8). The resulting value is approximately 10^{141} .
- 2) We added new sentences to the main text to describe the obtained EC values and provided references to Supplementary Notes or Methods sections where these calculations are detailed.
- 3) We compiled a comparative table that evaluates the performance of all three proposed PUF models against existing literature in terms of EC and other essential parameters (see Supplementary Table 3).

Please, see below the modified main text parts that describe the calculation of EC for all three of the considered PUF-based protocols (green color highlights newly added sentences):

- 1) For the first PUF protocol: *“It is important to acknowledge that, despite the distinct physical origins of the five selected PL features, there exists a slight correlation among them. Additionally, the uneven distribution of pixels (structures) within the QR code results in observable non-random relationships when comparing different maps of the same feature. These correlations ultimately diminish the overall degrees of freedom in our PUF label, thereby reducing its true encoding capacity. Taking into account these inevitable but acceptable correlations and the HD gates set for authentication, we assessed the number of all the possible unique PUF labels distinguishable by our validation algorithm: $\sim 10^{54}$ (Methods). This value is enough for the successful use of the label [Arppe2017Apr]; if necessary, it can be boosted by increasing the mapping resolution.”*

2) For the second PUF protocol: *“Figure 4e shows the distribution of the number of matches obtained during intra- and inter-comparison of 60 captured images. ~~There is a considerable gap between these two sets of values, which justifies the proposed concept.~~ There is a considerable gap between these two sets of values, which allow us to determine a suitable threshold value, ensuring a wide range of accuracy, even for images captured in diverse conditions. Furthermore, the encoding capacity of this PUF model is estimated to be about 10^{141} (Supplementary Note 8 and Supplementary Fig. 16).”*

3) For the third PUF protocol: *“To ensure the uniqueness and randomness of the generated embedding keys, we evaluated them using the NIST randomness test suite⁶², yielding positive results (Supplementary Note 13 and Supplementary Table 2). Furthermore, the computed information entropy values for each embedding coordinate indicate a high degree of unique information saturation, along with complete uniformity and unpredictability of the obtained keys (Supplementary Note 14 and Supplementary Fig. 20). Finally, the estimated encoding capacity of the embedding space is significant, reaching 10^{280} (Supplementary Note 15 and Supplementary Fig. 21).”*

Comment 3. Another concern is the fabrication process, which involves fs-laser processing, contributing to high production costs.

Our reply.

We thank the Reviewer for highlighting this important concern. We would like to address the raised issue by considering several following points.

Firstly, regarding laser-assisted fabrication in general, it is important to note that laser technologies are recognized as "green" technologies, offering several advantages such as material selectivity, precision treatment, rapid and targeted scanning speeds, and the elimination of chemical reagents. Consequently, the total cost of ownership for laser fabrication lines can be sufficiently low in certain scenarios. For instance, a comparison of wet-etching and laser-patterning production lines for 50-inch plasma displays revealed that, over a three-year period, a laser production line, despite its higher initial cost, could save up to \$160 million [1]. Thus, in general, laser fabrication technologies are cost effective (in the long term) and can even beat traditional technologies in some manufacturing processes.

Secondly, while it is true that femtosecond (fs) lasers typically have a higher price than continuous wave (CW) or nanosecond (ns) and microsecond (ms) lasers, they can provide significant advantages in specific applications where precision is crucial. For example, in scenarios requiring post-processing after conventional laser treatment or selective targeting of multilayered systems, fs-lasers can deliver beneficial results. A return on investment (ROI) analysis for femtosecond laser cutting of nitinol stents indicated that *"post processing costs plunged from \$11.01 per unit with a ms fiber laser to a mere \$2.08 per unit with the fs-laser. This reduces the annual post processing costs from more than a million dollars a year to just over \$200,000. Even with a capital outlay of nearly three times the ms fiber laser, the fs-laser's payback period is a mere 12 months – well worth considering"* [2].

Therefore, it is not surprising that the global market for fs lasers is experiencing rapid growth, with a projected compound annual growth rate of 8.67% from 2024 to 2033 [3]. This growth has led to an increase in the number of companies offering industrial fs-laser systems, stimulating greater market competition and driving down prices. A notable example of fs laser integration in industry is in ophthalmology. A decade ago, the use of fs lasers there was met with skepticism due to their costs [4]; however, they are now widely employed in myopia treatments, such as in SMILE technology [5].

Focusing on the fabrication process employed in our work, we adopted a single-step, high-throughput fs-laser-printing approach without any chemical post-treatment. This method requires minimal additional consumables and is characterized by a long warranty period for the equipment used. Consequently, the primary contributor to the cost of our PUFs is the equipment expenses, which diminishes over time due to the long service life and mass production. To provide some

evidence for this thesis, we have calculated the total cost of fabricating our PUF label, taking into account both material and equipment costs (see Supplementary Note 17). The resulting price of the proposed PUF security label, which is on the order \$0.3, is acceptable (compared with some other PUFs presented in the literature, for example, see Ref [6] or Supplementary Table 3), which indicates that fs-laser fabrication is indeed a viable option for practical applications.

To provide a Reader with the practical aspects of our work, as well as to deliver all the important points that we made when answering the first and the third Reviewer's questions, we added two following paragraphs to the Discussion section of the manuscript.

“One of the key aspects that distinguishes the presented work is our approach to addressing the structural variations in fabricated Au/Si particles. Since the direct analysis of this internal randomness (with characteristic sizes of 20 nm) requires tedious TEM-based techniques, we proposed using the particles' PL spectra as an alternative, highly capacious source of unclonable keys. In support of this method, we investigated how the multi-resonant nature of our particles establishes a strong linkage between their internal composition and the spectral features of the emitted PL. We have shown that each PL spectrum contains a wealth of unique spectral information, leading to an exceptionally high storage density (i.e., the amount of data extracted from a PUF per unit area). Indeed, in our latest protocol, which employs machine learning to encode individual PL spectra, each square micrometer of the label effectively stores 3,720 random bits (Supplementary Note 15). This represents an exceptional storage density that is 2-3 orders of magnitude greater than that of other optical PUFs (see the calculation of this parameter for all of the presented PUF concepts in Supplementary Note 16). Ultimately, the Supplementary Table 3 demonstrates that we have successfully downscaled the characteristic randomness of our PUFs.

Considering the potential practical value of our PUFs, it is important to emphasize their key advantage: high-entropy spectral responses controlled by nanoscale structural randomness. This concept provides the highest level of protection, not only in the immediate future but also over many decades to come. This is particularly crucial as we enter an era where traditional PUFs, which rely on microscale spatial randomness, will become increasingly vulnerable due to advancements in precise micro-manipulation techniques. Although in our approach demonstration we have used costly laboratory equipment, the long-term implementation will substantially reduce expenses for each individual PUF label (see Supplementary Note 17 for our cost estimations). Additionally, the rapid advancements in industrial fiber-optic fs-lasers and spectrometers are expected to further enhance the viability of our technology (for example, in Supplementary Note 18 and Supplementary Fig. 22 we showed that our PL measurement setup can be greatly simplified by employing a low-cost commercial spectrometer). Another important point is the environmental stability of our labels; when encapsulated in a polydimethylsiloxane (PDMS) protective layer, they demonstrate robust performance against a variety of typical external disturbances (see

Supplementary Note 19 and Supplementary Figs. 23-24). With all of the above, we believe that our approach is going to find its industrial niche in the future.”

We also added new supplementary materials, in particular, Supplementary Notes 16-19 (“On the concept and calculation of storage density”, “Calculation of the overall cost of a single PUF label”, “PL measurements with an industrial optical fiber spectrometer”, “On the environmental stability of proposed PL-based PUFs”) and Supplementary Figures 22, 24 (“Testing an industrial optical fiber spectrometer for possible PL measurement”, “Testing environmental stability of the PL spectra-based PUFs”), and Supplementary Table 3 (“The performance of several prominent optical PUFs in terms of critical and overall PUF size, storage density, encoding capacity, and acquisition time for a single optical measurement”).

References used in the answer:

- [1] https://www.photonics.com/Articles/Saving_Money_with_Laser_Processing/a32560
- [2] <https://amadaweldtech.com/blog/update-on-roi-for-disk-femtosecond-lasers/>
- [3] <https://www.custommarketinsights.com/report/femtosecond-laser-market/>
- [4] <https://www.healio.com/news/ophthalmology/20120331/steep-initial-costs-associated-with-femtosecond-laser-for-cataract-surgery>
- [5] <https://www.zeiss.com/meditec/en/products/refractive-lasers/femtosecond-laser-solutions/smile-minimally-invasive-eye-surgery.html>
- [6] Zhang, Tongtong, et al. "Multimodal dynamic and unclonable anti-counterfeiting using robust diamond microparticles on heterogeneous substrate." *Nature Communications* 14.1 (2023): 2507.

REPLY TO THE FIRST REVIEWER

We sincerely thank the Reviewer for their kind comment review and putting so much effort and time into reviewing our manuscript.

REPLY TO THE SECOND REVIEWER

We sincerely thank the Reviewer for their kind comment review and putting so much effort and time into reviewing our manuscript.

REPLY TO THE THIRD REVIEWER

We sincerely thank the Reviewer for their kind comment review and putting so much effort and time into reviewing our manuscript.