

A transient carbon nanocoating for improved processing efficiency of copper during laser powder bed fusion

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ARTICLE INFO

Keywords:

Laser powder bed fusion (LPBF)
Copper
Laser absorption
Powder coating
Defocused laser strategy

ABSTRACT

Laser Powder Bed Fusion (LPBF) of copper faces significant challenges due to copper's high thermal conductivity and low laser absorptivity, leading to melt pool instability, excessive spattering, and poor part quality. To address these issues, this study introduces a novel transient nanocoating strategy that temporarily enhances laser absorption while being designed to vaporise during processing to preserve the purity of the copper. Combined with a defocused laser strategy, this approach achieves a more uniform energy distribution, resulting in a stable melt pool, controlled vapour formation, and minimal spatter. The effectiveness of this synergistic strategy is validated through static and dynamic absorptivity measurements. For the static absorptivity, the coated copper powder absorbs 67% of the input laser power, 3.5 times higher than untreated copper, achieving the highest absorptivity enhancement (147% per 1 wt% of additive) reported to date. The dynamic absorptivity is also improved from 12% for untreated copper to 51% for coated copper powder. These advancements not only establish a transformative pathway for the LPBF of copper and other highly reflective metals but also highlight the approach's potential to enhance energy efficiency and promote sustainable manufacturing practices in advanced material processing.

1. Introduction

Copper is an essential material in the electrification of transport and the global transition toward decarbonisation, due to its exceptional electrical conductivity, high thermal conductivity, excellent ductility and workability [7]. The demand for copper components with complex geometries is particularly high in the energy sector and applications such as windings [32], antennas [17], and heat sinks [30], which rely on an improved surface area or volume for optimal performance. Laser Powder Bed Fusion (LPBF) is a leading metal additive manufacturing (AM) technique capable of fabricating complex shapes with high dimensional accuracy. However, its application to copper presents significant challenges due to copper's high reflectivity at near-infrared wavelengths (absorptivity $\leq 10\%$ at 1060–1080 nm [34]) and high thermal conductivity. These properties limit the absorption of laser energy, leading to unstable melting effects such as spattering, balling, and lack of fusion defects [15] [23]. Effective absorptivity of laser energy is, therefore, a critical factor in overcoming these challenges and achieving high-density copper components.

Several strategies to mitigate this problem have been pursued, including: (1) shorter-wavelength lasers, such as green or blue, show better absorptivity in copper but are costly and less accessible [18][41]; (2) ultrahigh-energy lasers, increasing incident energy but can be difficult to maintain (damage to optical components) and destabilise the melt pool [14]; (3) alloying, mixing or coating copper powder with absorptive materials, such as carbon-based materials [6], Cr [36] can improve laser absorption but often compromises the intrinsic properties of copper. Even the addition of less than 0.1 wt% alloying elements can significantly decrease the electrical conductivity of copper [1], making these strategies unsuitable for applications requiring high-performance copper [11]; and (4) topography engineering on powder surface by etching process achieved 70% higher absorptivity without introducing additives [38], but the heavy reliance on corrosive etchants like HCl and FeCl₃ also introduces environmental concerns.

To prevent the above issues while achieving effective absorption, we propose a novel transient nanocoating strategy on copper powder in this study. Polydopamine (PDA) is a nanoscale, bio-inspired material that can be uniformly coated onto virtually any substrate in a sin-

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<https://doi.org/10.1016/j.matdes.2025.114552>

Received 11 February 2025; Received in revised form 21 July 2025; Accepted 8 August 2025

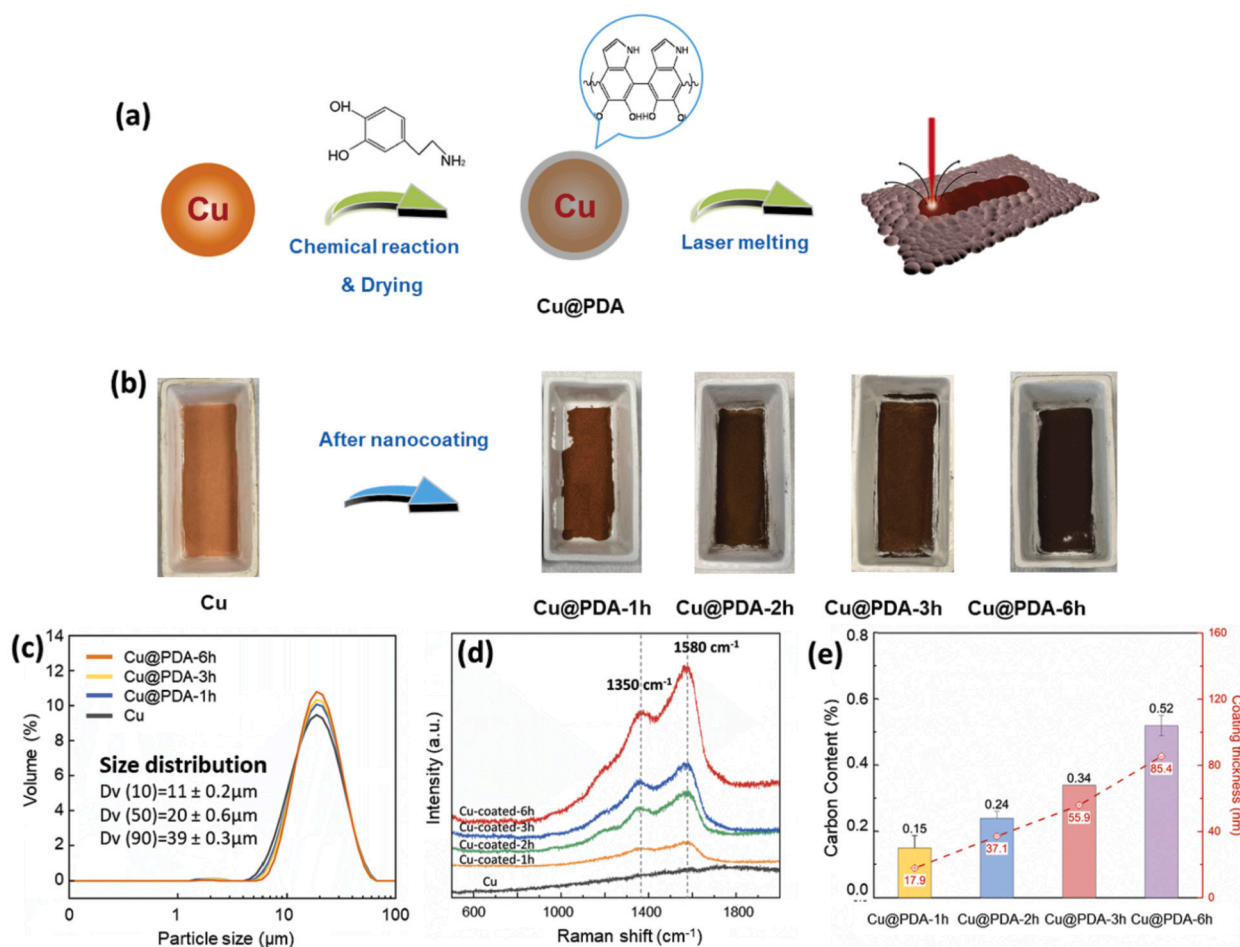


Fig. 1. (a) Schematic of the nanocoating process; (b) Colour changes of the powder particles under different coating process time; (c) Powder size distribution; (d) Raman shift of different powder particles; (e) Carbon content measured by carbon analyser.

gle step through an environmentally friendly polymerisation process. PDA has a well-documented photothermal effect, giving it high broadband absorption; a property already harnessed in applications such as infrared therapy [2,49]. Critically, PDA undergoes thermal decomposition at temperatures around 300 °C. This allows it to act as a transient absorption-enhancing coating that can be completely vaporised by the high-energy laser during the LPBF process, thus preventing the introduction of impurities and preserving the intrinsic properties of the copper. This approach circumvents the drawbacks of previous methods, offering an innovative and effective solution to the challenge of laser absorption in copper while preventing the matrix impurity.

Although increasing absorptivity is crucial, it is equally important to understand and measure dynamic absorptivity. This is challenging because the static absorptivity of the powder doesn't fully explain the dynamic one during the LPBF process. The effective absorption of laser energy in a dynamic environment is influenced by various complex factors, including phase changes (i.e., solidification and melting) [12], temperature gradients, and the formation of vapour and spatter [33]. Recent studies have shown that real-time absorption is also affected by factors such as material oxidation [10] and the stability of added nanoparticles (NPs) [25][16], which further complicate energy dynamics during the process. Given these complexities, quantifying dynamic absorptivity is vital for optimising process parameters and improving as-built quality. Although advanced measurement techniques, such as calorimetry or reflectometry [29], have been developed and applied to capture real-time absorption in commonly used materials like stainless steel [20] and nickel alloy, there remains a significant gap in the research on more challenging materials like copper.

To address the two major issues, namely the lack of reliable methods to enhance copper absorptivity and the need to effectively assess these methods, this study focuses on exploring both areas. An absorptivity-enhanced nanocoating on copper powder is proposed, combined with a defocused laser strategy. This nanocoating is uniquely designed to vaporise upon laser interaction, significantly enhancing energy absorptivity while minimising the introduction of impurities into the melt pool. To the best of our knowledge, this is the first study to use this transient nanocoating strategy for copper in LPBF while simultaneously integrating advanced in-situ absorptivity measurement techniques to evaluate real-time laser absorption. This comprehensive approach not only advances the understanding of the absorption dynamics of LPBF copper but also provides adaptable solutions for other highly reflective metals, paving the way for more efficient and sustainable AM processes.

2. Experimental details

2.1. Preparation of nanocoating

Copper powder particles were acquired from Goodfellow Metals Ltd., featuring a nominal size under 50 μm, with D10 at about 11 μm, D50 at 20 μm, and D90 at 39 μm (shown in Fig. 1 c). Dopamine hydrochloride (DA), tris(hydroxymethyl)aminoethane (TRIS), and phosphate buffered saline (PBS) were purchased from Sigma Aldrich. A feasible one-step coating approach to form PDA coating was applied to the copper powder particles.

4g of copper powder particles were added to 100 ml TRIS-buffer and stirred magnetically for good dispersion. Then, DA was dissolved into

the solution and followed by stirring at room temperature for 1 h, 2 h, 3 h, and 6 h, with longer times expected to produce a thicker coating. These samples were labelled as Cu@PDA-1h, Cu@PDA-2h, Cu@PDA-3h, and Cu@PDA-6h, respectively. The colour of the solution gradually changed from transparent to pale brown and finally dark brown, indicating the formation of PDA. The coated powder particles were obtained through a repeated washing process: the suspension was sonicated for 5 minutes and then left to settle under gravity, allowing lighter PDA aggregates to remain near the surface. These aggregates were removed by decanting and pipetting. This washing step was repeated five times, during which the liquid gradually changed from dark brown to clear, indicating effective removal of excess PDA. Then the collected powder was vacuum dried at 60 °C for 5 h [21]. For flat surface characterisation, copper and silica substrates with dimensions of 1.5 × 1.5 cm² were attached to the wall of a beaker and coated with PDA using the same protocols. These coated substrates are referred to as Cu sub@PDA-i and Si sub@PDA-i, where i refers to the corresponding stirring time.

2.2. Laser powder bed fusion process

The LPBF experiments were performed in an argon gas environment using a Renishaw AM250 machine equipped with a modulated continuous wave Yb-fibre laser of 200 W and fitted with an InGaAs photodetector (Thorlabs PDA10CS2) that, in conjunction with a 1070 nm bandpass filter (Thorlabs FBH1070-10), measures the intensity of a segment of the laser beam as it traverses a mirror. The correlation between the photodetector measurements and the precise laser power P_{Laser} was quantified through a power calibration process utilising a power meter.

Round copper discs with a thickness of 500 µm and a diameter of 10 mm were used as substrates. A 100 µm thick layer of powder was spread manually on the substrate using a coating applicator. A series of 5 mm long single tracks was produced using varying laser power, scan speed (adjusted through exposure time and point distance), and laser diameter. All parameters are listed in Table 1.

2.3. Static and dynamic absorptivity measurement

To investigate the efficacy of the nanocoating on absorptivity, static absorptivity (i.e. on the bench) of powder was measured before LPBF and dynamic (in-situ) absorptivity was measured during LPBF for different types of powder. The static absorptivity of powder was measured at room temperature using an integrating sphere and InGaAs detectors (Thorlabs PDA10CS2) with 1070 nm bandpass filters (Thorlabs FBH1070-10), which corresponds to the wavelength of the laser used in a Renishaw AM250 system.

To measure the dynamic absorptivity during the LPBF process, a custom system was developed composed of a 3D-printed Ulbricht integrating sphere (UIS), an InGaAs photodetector (Thorlabs PDA10CS2) paired with a bandpass filter (Thorlabs FBH1070-10), and an optic fibre cable (Thorlabs M105L02S-B).

The UIS has an internal diameter of 120 mm and was coated internally with a high-diffuse white acrylic paint (with a measured reflectance of 91.4% at 1070 nm). An opening at the top allows the laser to enter the sphere and is offset such that the beam meets the sample at an angle of incidence of 6.4–9.0°. This offset prevents specular reflections from escaping through the inlet, minimising signal loss. A ø24 mm sample port with rectangular gas-flow apertures at the sides is located at the base of the sphere. The gas flow minimises plume effects on the signal and maintains conditions true to the normal LPBF process. The tangentially mounted optical fibre is shielded by an internal baffle that blocks any direct or near-specular ray from the sample region. The area of all openings accounts for 1.6% of the interior surface, well below the 5% limit for accurate spatial integration. The photodetector signal was calibrated using N-BK7 diffuse reflectors with a protected gold coating of known reflectance (Thorlabs DG10-220-M01 and DG10-600-M01). The sphere was cleaned with compressed air and a lint-free optical cloth

Table 1

Parameters used for this study.

Laser parameter	Value
Power (W)	140, 160, 180, 200
Exposure time (µs)	100, 200, 400, 600
Point distance (µm)	10
Speed (mm/s)	16.67, 25, 50, 100
Defocus distance (mm)	0, -2, -4, -6

after every fourth test. The calibration was checked throughout the experimental program, with a variation of less than 1%.

During the experiment, the laser beam enters the UIS through the inlet opening, illuminates the sample at the powder bed level, and any reflected light is captured by the UIS and then transmitted to the photodetector through the optical fibre cable. The dynamic reflectance P_R and dynamic laser power P_{Laser} were measured during the laser processing of various powders using the parameters listed in Table 1. All experiments were performed in triplicate and the results were averaged. By applying the conservation of energy, the dynamic absorbed power P_A was determined using the equation:

$$P_A = P_{Laser} - P_R \quad (1)$$

The dynamic absorptivity A was calculated by normalising the absorbed power P_A against the laser power P_{Laser} :

$$A = P_A / P_{Laser} \quad (2)$$

2.4. Characterisation

The particle size distributions of all powder samples were measured using the Mastersizer 3000 (Malvern). The carbon content of the powder and the as-built parts was tested using a carbon analyser (Horiba EMIA-920V2). The powder morphology was analysed using a scanning electron microscope (SEM, Tescan Mira) at 15 kV. Raman spectra of powder were collected using a 532 nm excitation laser with a 100× objective with an 1800 g/mm diffraction grating using a LabRAM HR Evolution system (HORIBA). Each spectrum obtained was an average of 3 measurements. The coating thickness on the flat substrate was measured with a stylus profiler (KLA Tencor D-600 Profiler). Each sample was measured at least three times at different positions on average. The thickness of the powder coating was evaluated using transmission electron microscopy (TEM, JEM-2100Plus) at an acceleration voltage of 200 keV, respectively. For each image, at least five measurements were taken for the average thickness. To prepare samples for TEM, a small amount of the coated powder was dispersed in deionised water and sonicated for several minutes to reduce agglomeration. A few microlitres of the diluted suspension were then drop-cast onto a 300-mesh gold TEM grid with carbon film. As the samples were analysed in powder form and the coating was very thin (20–90 nm), further thinning was not required. The carbon content (wt%) of the coated powder was measured using a carbon analyser (Horiba emia-920v2), with a detection limit of 0.00001% (0.1 ppm).

All topographic information of the tracks, including the height, width over the substrate and surface roughness, was acquired using a laser scanning microscope (Olympus, OLS5100). Continuous single-track samples were further cut perpendicular to the track direction and cold-mounted in epoxy resin. The samples were polished to a 1 µm diamond suspension and etched for 15 seconds in a solution consisting of 2.5 ml of hydrogen chloride, 75 ml of C₂H₅OH, and 3.5 g of FeCl₃. The cross-sectional microstructure and melt pool were observed using an SEM (Tescan Mira) at 15 kV. Optical microscopy (OM) to identify pores and non-dense regions. Image analysis software was then used to calculate the relative density by quantifying the area fraction of pores in each sample. The relative density of as-fabricated samples was calculated by quantifying the area fraction of defects relative to the solid

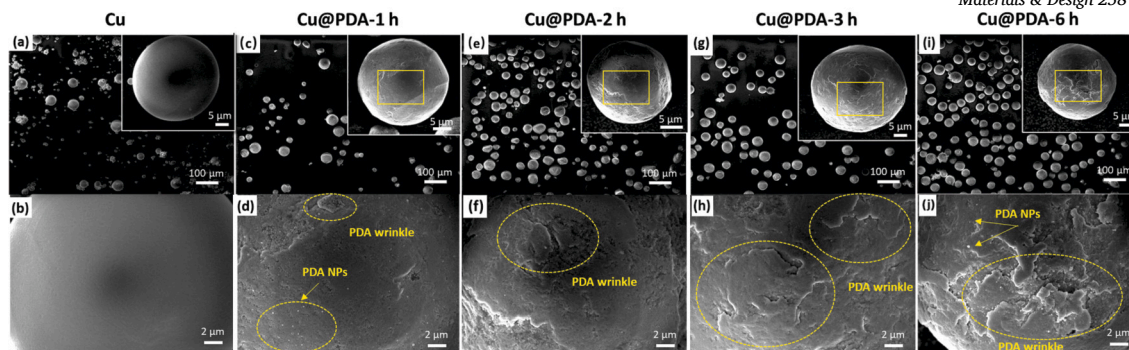


Fig. 2. SEM images of powder surface from different powder: (a-b) Cu, (c-d) 1 h, (e-f) 2 h, (g-h) 3 h, (i-j) 6 h.

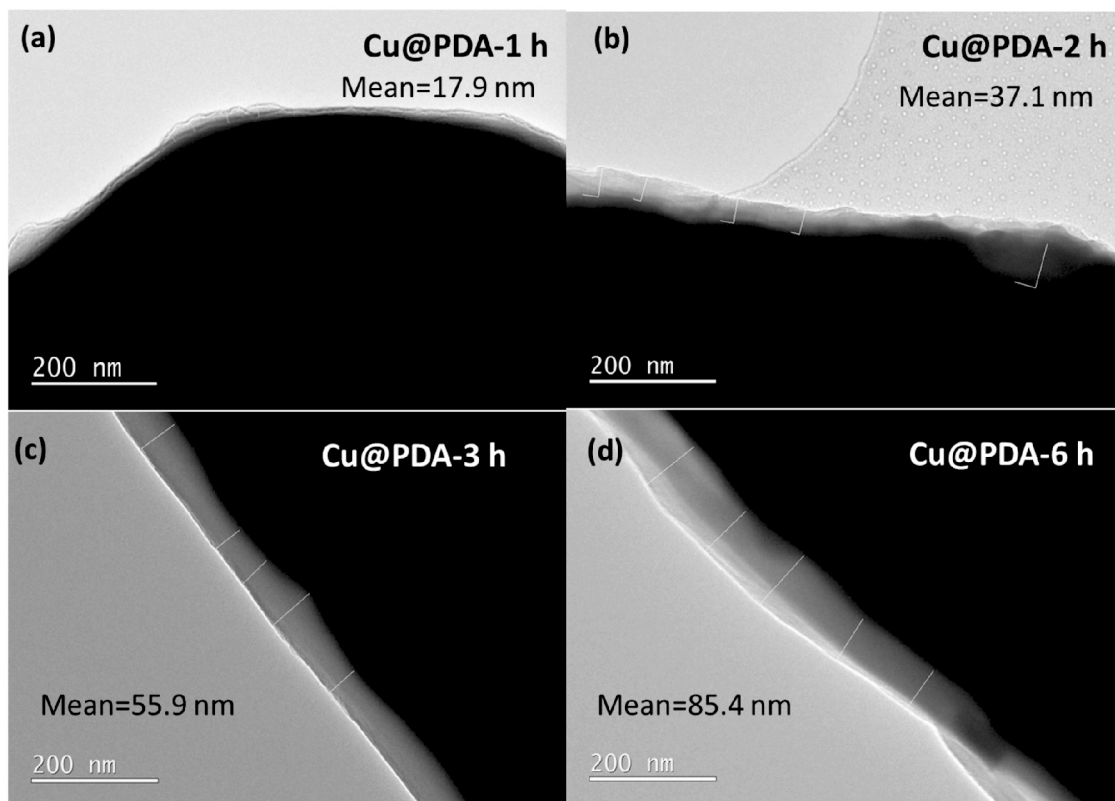


Fig. 3. TEM images of nanocoating thickness under different coating process time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 6 h.

matrix in cross-sectional images using ImageJ. Five samples were measured for each condition, and the average value was reported in Table 2.

3. Results and discussion

3.1. Powder coating characterisation

After coating, the powder particles retain their spherical shape without obvious deformation or bonding, as demonstrated by the SEM results. The size distribution of the coated powder is also similar to that of the original copper powder (Fig. 1 c). The more pronounced peak concentration observed may be attributed to the removal of a small fraction of fine particles after the rinse process. Since the coating thickness (nanometre range) is significantly smaller than the copper powder size (up to 50 μm), its effect on the overall particle size can be negligible. These powder features ensure the essential flowability required for powder spreading. Morphological observations show increased wrinkles and adhesion of PDA NPs to the powder surface with longer coating duration. PDA forms through the self-polymerisation of dopamine, a process

in which polydopamine can either deposit as a continuous film on substrates or self-assemble into nanoparticles in solution, depending on the reaction conditions. Extended coating duration promotes the formation and attachment of excess nanoparticles as well as surface wrinkling, leading to increased surface roughness (demonstrated in Fig. 2 and Fig. 4 a-c).

A moderate coating process time (3 h) resulted in a more homogeneous coating and fewer PDA aggregates on powder particles. Increasing the coating process time to 6 h, the wrinkled surface and the amount of adhered PDA NPs increase significantly. This trend aligns closely with the findings of Lee et al. [21] regarding PDA coating on Si substrates. More thickness results will be discussed in Section 3.2.

Raman spectroscopy (Fig. 1 d) validates the presence and composition of the PDA coating on the powder. Two broad bands at approximately 1350 and 1580 cm^{-1} shown in all Cu@PDA samples are attributed to the stretching and deformation of aromatic rings of PDA [9], indicating the success of surface coating on copper powder. These peaks become sharper and more pronounced with an increase in the PDA thick-

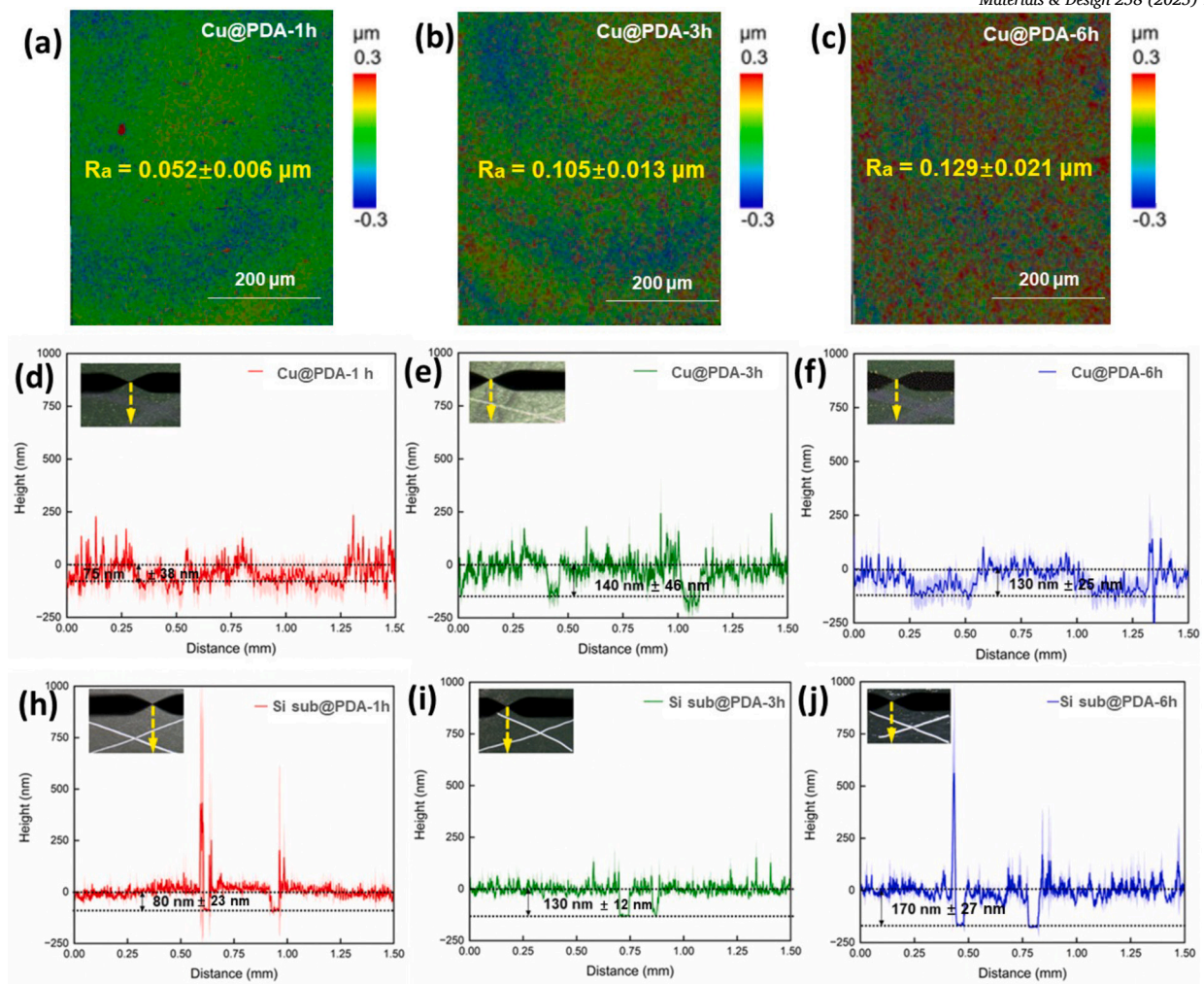


Fig. 4. Surface roughness of different coating on flat substrates: (a) Cu@PDA-1h, (b) Cu@PDA-3h, (c) Cu@PDA-6h. Film thickness of different coating on (d-f) copper substrates and (h-j) silica substrates.

ness due to a longer coating process time, while no peaks are detected on pure copper powder.

Tailoring the thickness of the PDA coating is crucial to achieving the desired absorptivity during the laser powder bed fusion process. According to existing studies [4][5], the thickness of PDA coating can be finely controlled within the nanoscale by adjusting the reaction time and concentration. Fig. 3 shows representative TEM images of PDA-coated Cu powder with different coating process time. The TEM images showed that PDA coating is uniformly applied on the surface of copper powder, forming a core-shell structure. It was found that the average coating thickness gradually increased from approximately 17 nm to 85 nm as the coating process time increased from 1 h to 6 h. This finding is also well consistent with other reports that the thickness of PDA coatings usually ranges from 20 to 100 nm under the same conditions [31].

To demonstrate the reproducibility and uniformity of the PDA coating, we extended the identical coating process to copper and silica substrates (Fig. 4). As expected, the coating thickness increased with the duration of the coating process, and concurrently, surface roughness also increased from 0.052 μm to 0.129 μm (Fig. 4 a-c) due to the aggregation of PDA NPs [22]. This higher surface roughness further corroborates the previous SEM findings of Fig. 2. A slight difference in measured thickness is observed between the two substrates, which can be attributed to the inherent variations in substrate roughness and hardness. The measurements on silica substrates are considered more robust as a result of their high hardness, which enables the creation of precise and narrow scratches without compromising the substrate's integrity.

The coating thickness and roughness on flat substrates are observed to be higher than those on powder particles. This may be attributed to the increase in aggregation on flat substrates, which was demonstrated before that PDA aggregates near the flat substrate were more easily trapped and embedded in the PDA coating [8][44].

3.2. Static and dynamic absorption properties of the nanocoated powder

To fully characterise the absorptivity of the powder, two types of measurement were performed, static and dynamic. The static measurements were performed on the bench, with a low-power illumination source such that any temperature changes in the powder were negligible. The dynamic measurements were performed in-situ, with the processing laser heating and melting the powder as would happen under normal processing conditions. To perform the dynamic measurements, a special apparatus was devised, as shown in Fig. 5 a. The static absorption measurements (shown in Fig. 5 b), reveal that the nanocoated copper powder exhibits significantly enhanced laser absorption. The level of absorptivity increases in proportion to the coating process time. In particular, the Cu@PDA-6h sample exhibits the highest absorptivity rate, measured at 67%, which is 3.5 times increase relative to that of the untreated copper powder. The Cu@PDA-3h achieves a comparable absorptivity rate to Cu@PDA-6h and therefore Cu@PDA-3h has been selected as the optimal coating condition for production efficiency. The slower increase in absorptivity at longer coating durations is due to the saturation of available surface sites. As the powder surface becomes

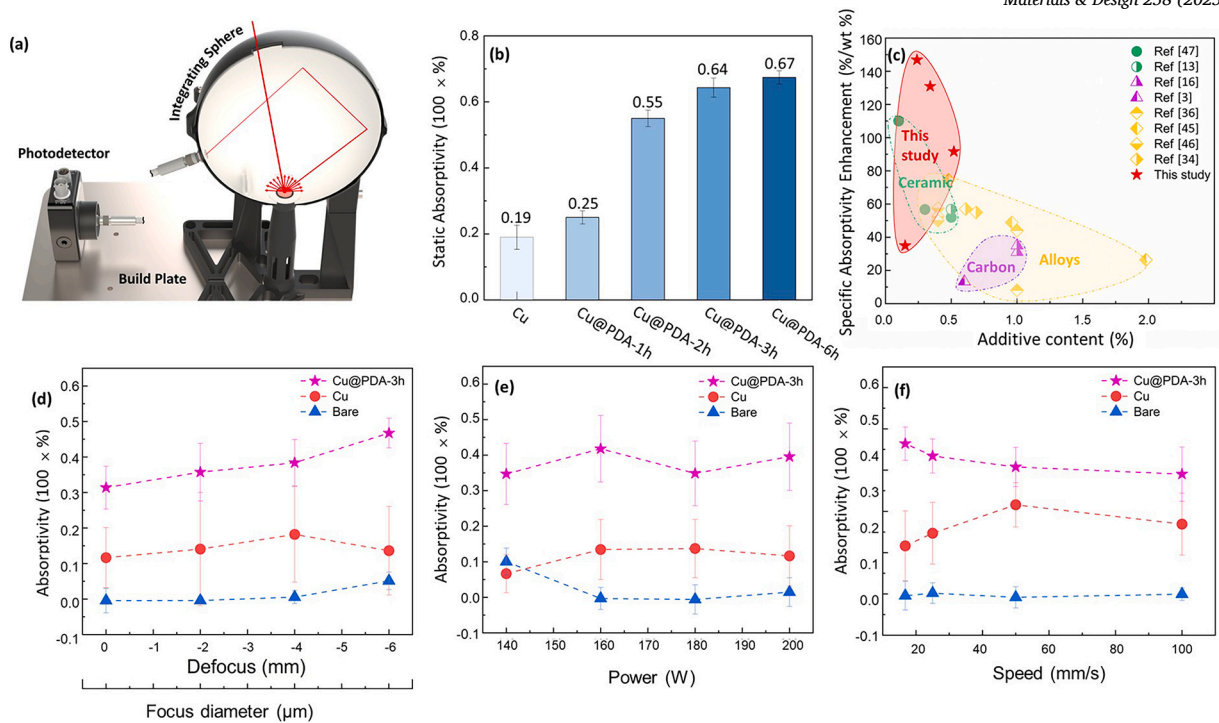


Fig. 5. (a) The schematic of in-situ absorptivity measurement system, integrating a photodetector and an integrating sphere to accurately capture the laser reflectivity during LPBF; (b) static laser absorptivity with different coating process time at the wavelength of 1070 nm; (c) comparison of enhancing efficiency on laser absorptivity of Cu powder between this study and other reported data [48] [13] [16] [3] [37] [46] [47] [35]; The dynamic absorptivity during LPBF as a function of: (d) defocus distance/laser spot diameter (laser power = 200 W, scan speed = 16.67 mm/s); (e) laser power (scan speed = 16.67 mm/s, defocus distance = 0 mm); and (f) scan speed (laser power = 200 W, defocus distance = 0 mm).

fully covered, further PDA coating growth is restricted, resulting in a self-limiting thickness effect [21]. These results are consistent with the thickness data in Fig. 3. Fig. 5 c evaluates static absorptivity enhancement efficiency for PDA-coated powder, quantified as specific absorptivity enhancement per 1 wt% of additive, and compares it with data from studies on different additive like ceramics, alloys, and carbon materials. The results demonstrate that PDA-coated powder presents superior absorptivity efficiency up to 147% with minimal additive incorporation, highlighting the potential as an effective absorptive agent for LPBF.

However, the static absorptivity measurements do not accurately reflect the true in-process absorptivity due to the transient, complex laser-material interactions occurring during powder melting. To explore the effect of these interactions on dynamic absorptivity, laser diameter, laser power, and scanning speed were varied (shown in Fig. 5 d-e). The results show that Cu@PDA-3h powder consistently outperforms uncoated copper under all test conditions. Specifically, increasing the laser diameter improves absorptivity for all samples, with the Cu@PDA-3h powder achieving the highest absorptivity of up to 51%, at a laser diameter of 218 μm , which is nearly 5 times greater than uncoated copper. This absorptivity achieves the performance in the study where a 500 W laser power was utilised at a scanning speed of 100 mm/s [23]. This phenomenon illustrates the necessity of adjusting the laser diameter to effectively utilise the laser energy for powder melting rather than powder spattering. The results demonstrate that, although laser power has minimal impact on absorptivity below the 200 W threshold, the nanocoating remains effective beyond this power range, indicating its superior performance and adaptability. As scanning speed increases, a general decrease in absorptivity is observed, yet PDA-coated powder still maintains superior dynamic absorptivity, up to 36%, especially at lower speeds. These findings collectively highlight the feasibility of this nanocoating strategy in maintaining high laser absorption efficiency across different processing parameters. Section 3.5 will provide further discussion for the mechanisms at play.

3.3. Track morphology and melt pool microstructure

The height profile of the tracks built on the discs is presented in Fig. 6 a-d, which shows a clear progression in material deposition on the bare copper discs, uncoated copper powder-covered discs, Cu@PDA-1h and Cu@PDA-3h powder covered discs, all melted under identical conditions (200 W, 600 μs , 10 μm). The bare disc shows no trace of melting, whereas the uncoated copper powder-covered disc shows some evidence of deposition, with scattered balling visible. However, this loose balling fails to bond with the substrate and detaches easily. Conversely, the nanocoated powder, especially Cu@PDA-3h, exhibits significantly enhanced formation quality, featuring more continuous and well-defined tracks despite different parameters. The Cu@PDA-1h sample slightly improves track continuity compared to uncoated Cu, but the tracks remain discontinuous, suggesting that the coating thickness is too thin. This highlights the importance of adequate coating thickness in enhancing track formation quality.

The effectiveness of the processing parameters, such as power, laser diameter, and scanning speed was investigated (shown in Fig. 6 d-f). Increasing power and laser diameter or reducing scanning speed leads to more stable tracks, resulting in an observable increase in track width and a slight elevation in track height (shown in Fig. 6 h-i). Within a power limit of 200 W, the laser diameter is the most critical factor. Increasing the laser diameter significantly enhances the continuity and stability of the track, resulting in more uniform material deposition and up to 1.5 times the increase in the width of the track. This phenomenon may result from a larger laser spot diameter (shown in Table 2) and corresponding lower energy density, therefore it weakens the spattering and promotes the material deposition. This highlights the importance of fine-tuning these parameters, particularly the laser diameter, to optimise the nanocoated powder performance.

Close observation of the cross section of the melt pool revealed that the width and depth are proportional to the laser diameter, and all melt pools present a semicircular shape (shown in Fig. 7), which corresponds

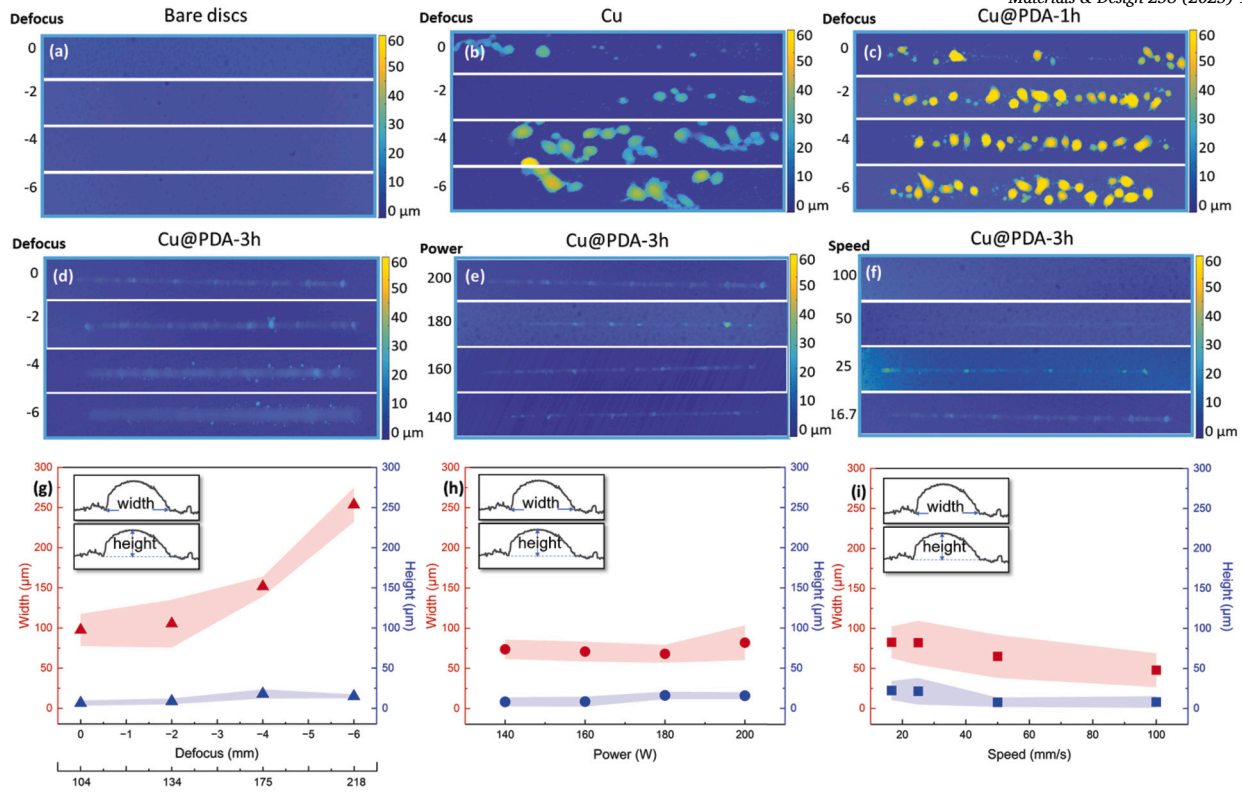


Fig. 6. The melt track profile of (a) bare copper discs, (b) Cu, (c) Cu@PDA-1h and (d) Cu@PDA-3h, using laser power of 200 W, exposure time of 600 μs , point distance of 10 μm and different defocus distances/laser diameters; The track profiles of Cu@PDA-3h under (e) varying laser power (scan speed = 16.67 mm/s, defocus = 0 mm) and (f) varying scan speed (laser power = 200 W, defocus = 0 mm). All height measurements are in microns. (g)–(i) Track width and height measurements of Cu@PDA-3h, corresponding to the melt track conditions shown in (d)–(f).

Table 2

Laser diameter and relative density under different defocus distance/laser diameters.

Defocus distance (mm)	Laser diameter (μm)	Laser energy density (W/mm^2)	Density(%)
-6	218	5383	98.79 $\pm$ 0.49
-4	175	8315	97.65 $\pm$ 0.64
-2	140	13086	95.31 $\pm$ 0.52
0	104	23544	92.42 $\pm$ 1.70

Laser energy density is calculated using the maximum power of 200 W. Density measurements were performed on parts fabricated at 200 W laser power and 16.67 mm/s scan speed.

to the conduction mode. Generally, the width of the melt pool is less affected by laser diameter due to the reduction in energy density [28]. However, a significant increase in width was observed with increasing laser diameter in this study. While the nanocoating enhances absorption of the powder, it also results in a larger melt pool plume as the coating is vapourised. With a tightly focused spot (smaller laser diameter) and high energy density, intense vapour plume pressures are generated, increasing vaporisation-induced spatter and denudation compared to an uncoated powder. This result is further demonstrated by the powder bed image in Fig. 9, which shows an increased number of spatter particles around the track at a defocus distance of 0 mm. Due to melt pool instability under this condition, the lowest density of 92.42% was obtained compared with other defocus settings. Conversely, when a defocused spot (larger laser diameter) is used, the intensity and volatility of the vapour plume are reduced, resulting in a more stable melt pool and less denudation [42], with a nearly full density of 98.79% achieved at a defocus distance of -6 mm. Similar results were demonstrated by researchers using X-ray imaging that a larger beam spot size helps to reduce vaporisation even in conduction mode [45]. In this case, more energy is retained in the melt pool to form a larger solidified region. The mech-

anism by which the coating enhances absorption will be analysed in detail in Section 3.5.

Higher-magnification observations (Fig. 7. b-c) show well-defined and orientated cells (indicated by yellow arrows), and cellular dendritic structures (indicated by an orange arrow) in the melt pool. The cellular dendrites are oriented perpendicular to the borders of the melt pool or point out of the imaging plane, consistent with previous reports for LPBF-processed copper by Jadhav et al. [15]. Occasionally these cellular dendrites give the appearance of precipitates, but actually correspond to the tips of these cellular structures protruding from the plane [14].

3.4. Effect of coating thickness on carbon content

To investigate what happens to the carbon in the nanocoating after melting, tests on different types of powder and their corresponding as-built samples were conducted. The results can be found in the Table 3. For powder samples, it is apparent that as the coating process time for the nanocoated powder increases, the carbon content also increases from below the detection limit to a maximum of 0.52%. This trend aligns with the coating thickness of up to 85 nm, as illustrated in Fig. 1 e.

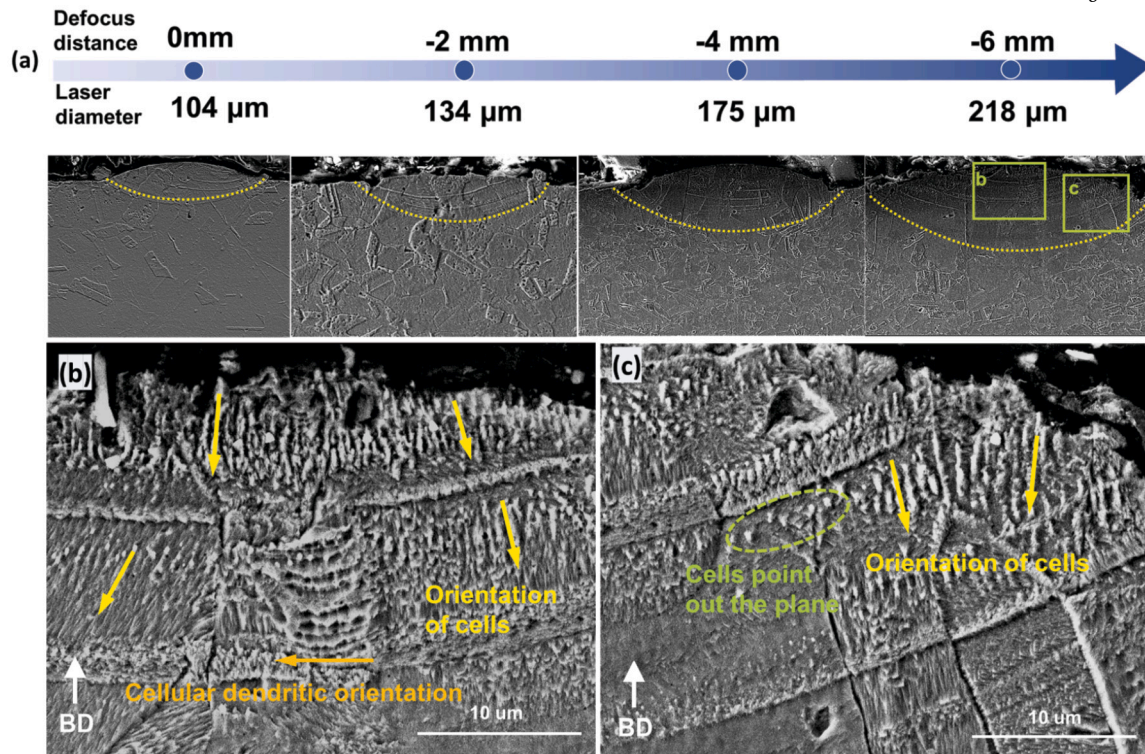


Fig. 7. (a) Secondary electron images of melt pools under different laser diameters of Cu@PDA-3h samples, with yellow dash indicating melt pool areas. (b-c) Secondary electron images with higher magnification showing cellular dendritic structures from areas with green rectangles.

Table 3

Carbon content (wt%) before (powder) and after (as-built samples) LPBF.

	Cu	Cu@PDA-1h	Cu@PDA-2h	Cu@PDA-3h	Cu@PDA-6h
Powder	0*	0.150	0.240	0.340	0.520
As-built	0*	0*	0*	0*	0.001

* Zero values indicate the carbon content is below the threshold for detection of 0.00001% (0.1 ppm).

For the as-built samples, the results revealed zero detectable carbon content, except for Cu@PDA-6h. The findings indicate that the absorptive nanocoating has been effectively eliminated after laser processing, without leaving carbon residues that could potentially compromise the integrity of copper. This carefully designed sacrificial nanocoating initially acts as a temporary absorptive layer, improving laser energy retention to promote powder melting and the creation of a stable melt pool, instead of reflecting the energy. Subsequently, under the localised, high-power laser conditions of LPBF, the PDA nanocoating undergoes complete thermal decomposition, releasing volatile by-products. Weng et al. [40] demonstrated that PDA begins to pyrolyse at 300 °C releasing gaseous products such as CO (or N₂), CO₂, and H₂O. The significantly high and transient temperatures achieved during LPBF (up to 2000 °C), which are sufficient to melt copper (melting point 1084 °C), are likely to drive the complete volatilisation of PDA without leaving residual carbon [43]. The decomposition behaviour of PDA coupled with the coating thickness control ensures the purity of the copper, as supported by no detectable carbon residues in the as-built samples (Table 3).

Similar studies using more stable carbon-based coating often reported residual phases or increased carbon/oxygen content in the final part. For example, the addition of carbon-based materials such as nanoparticles [14], carbon nanotubes [19] or graphene-oxide (GO) [39] has been shown to improve laser absorption and densification in copper powder during LPBF. However, the as-built parts exhibited significantly reduced properties compared to pure copper, with up to 40% lower mechanical strength, 60-90% lower electrical conductivity, and 40%

reduction in thermal conductivity, even with only 0.1 wt%. addition. These deteriorations were attributed to the segregation of residual nanotubes or nanoparticles and the formation of oxide layers along grain boundaries and interfaces. These findings highlight the significant advantage of our transient nanocoating, as it improves laser processability while maintaining the composition and integrity of the final copper samples.

3.5. The synergistic effects benefited from defocused laser and nanocoating

Fig. 8a provides an overview of the complex laser-material interaction involved in the LPBF process, which gives rise to phenomena such as vapour plume generation, recoil pressure, marangoni convection, and metal ejection. These physical dynamics are influenced by the laser energy distribution and the material's response, determining the stability of the melt pool and the formation of byproducts.

In a focused laser configuration (Fig. 8b), the laser energy is concentrated on a small area of the powder bed, rapidly raising the temperature of the copper particles beyond their boiling point. This localised overheating generates a strong vapour plume and recoil pressure, causing significant spattering and making the melt pool unstable [26]. Extensive spatter and subsequent denudation were captured by a camera. Most powder particles were expelled outward (as demonstrated in Fig. 9), with only a limited fraction of the powder undergoing melting, resulting in a confined melt pool [27]. The detailed LPBF process can be seen in the supplementary video. Comparable outcomes were corroborated by a study [6] that applied a graphite layer on the powder bed to enhance absorption.

In contrast, the laser-defocused strategy (Fig. 8c), with the focal point positioned above the powder bed, provides a broader energy distribution. This strategy reduces the peak energy density at the copper powder, thus lowering the intensity of metal vapour and recoil pressure, resulting in less spatter and denudation [24]. The wider energy distribution stabilises the melt pool and minimises thermal gradients by reducing Marangoni convection. The application of nanocoating further

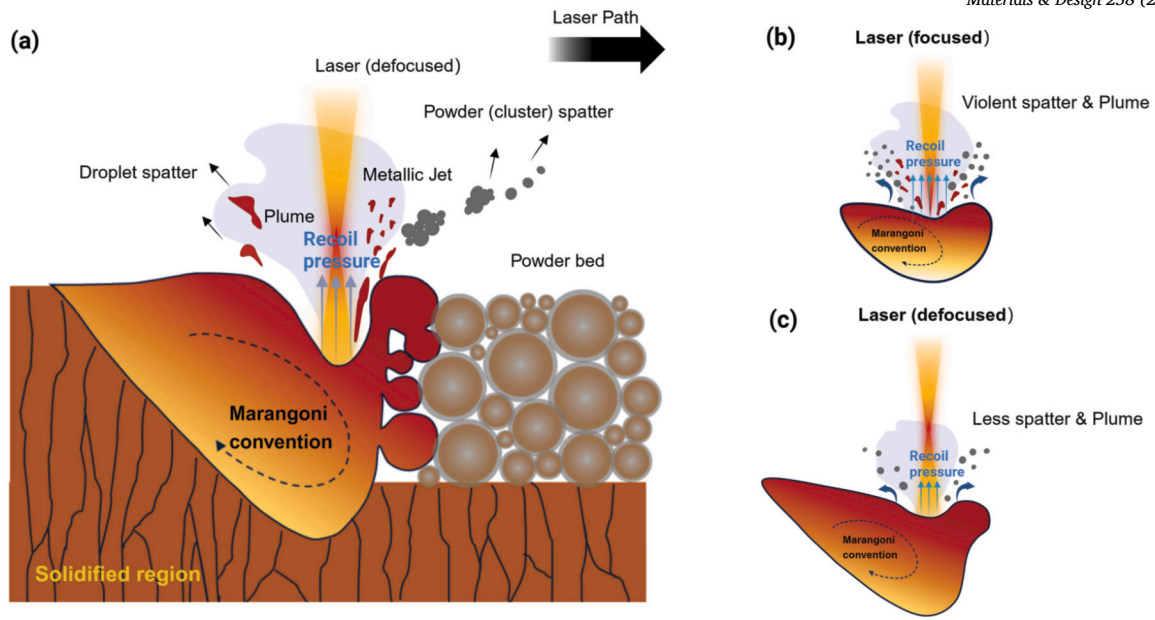


Fig. 8. (a) An overview of the melt pool dynamics during the LPBF process. Plume and spattering behaviour of the (b) focused laser condition and (c) defocused laser condition.

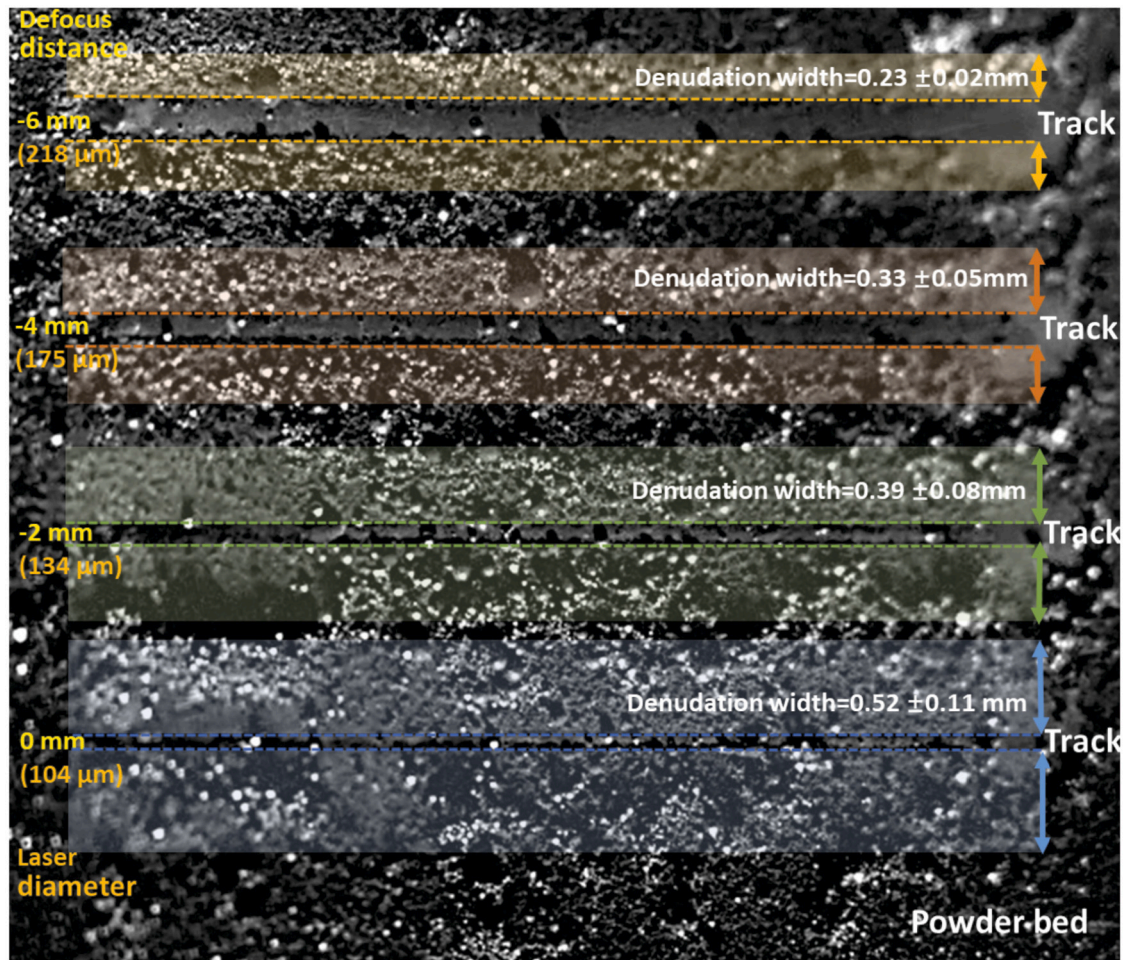


Fig. 9. Powder bed image captured by high-speed camera for different laser defocus conditions.

enhances the uniform absorption of the powder bed, which compensates for the reduced energy density due to laser defocus. This ensures most powder particles melt rather than disperse as spatter.

Compared to a tightly focused beam, the larger spot size reduces the precision of energy delivery, possibly impacting minimum feature sizes, surface quality and dimensional accuracy of the final part. Melt

pool depth is likely to be less, reducing the frequency of vapour-induced flaws (i.e. keyhole pores) but possibly increasing lack-of-fusion pores if unsuitable layer thickness or hatch spacing is used. Thermal gradients may also be reduced, meaning slower cooling and greater opportunity of larger grains to form.

When considering the overall process, this innovative combination of defocus strategy and absorptive nanocoating brings more advantages than disadvantages. In particular, their synergistic effects ensure efficient melting of the powder despite the lower energy density, optimise heat distribution, and reduce the risk of localised metal vaporisation and spatter, while maintaining the purity of the as-built samples.

4. Conclusions

In summary, this study addresses the challenges of processing copper with LPBF, including melt pool instability, excessive spattering, and how a powder coating can help mitigate the effects of high thermal conductivity and low laser absorption. The key findings are listed below.

1) The tunable nanocoating strategy applied in this study allows the regulation of the absorption performance by controlling the thickness of the nanocoating through adjustment of the coating process time. The optimal coating process time was found to be 3 hours, corresponding to a thickness of 56 nm, which achieved 67% absorption in static tests. Dynamic absorptivity was significantly improved from 12% to 51%.

2) Different laser parameters had varying effects on dynamic absorptivity, with the defocus distance/laser diameter having the most significant impact and the laser power having the less. This is likely because the enhanced energy absorption provided by the nanocoating outweighs the effect of laser power, minimising its influence.

3) The coated powder had significantly enhanced laser absorption and greatly improved build quality. Under optimal laser parameters (200 W laser power, 600 μ s exposure time, 10 μ m point distance, and a laser diameter of 175 μ m) the Cu@PDA-3h powder produced a consistent single track. In contrast, uncoated copper powder resulted in discontinuous balling that did not bond to the substrate under the same conditions.

4) The observed improvements are attributed to the synergistic strategy employed. The nanocoating strategy increased energy absorption by the melt pool, allowing more energy to be utilised in the melting process, while the defocused laser strategy reduced input energy density, preventing local overheating. This combination reduced by-products such as spatter and vapour, leading to a more controlled and stable melt pool evolution.

5) The nanocoating vapourised during processing with no detectable carbon introduced into the final melt track.

Overall, this comprehensive approach not only significantly enhances energy absorption and process stability but also provides a practical solution for the LPBF of copper with low-level laser power (200 W). Future research will focus on producing bulk specimens and characterising their properties to further confirm the effectiveness of this approach. It is also potentially adaptable to other highly reflective metals, paving the way for more efficient and reliable AM processes.

CRediT authorship contribution statement

Kaka Cheng: Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Investigation, Data curation, Conceptualization. **Zacharias Karavasilis:** Investigation, Data curation, Conceptualization. **Jamie Bell:** Investigation. **Sebastian Larsen:** Writing – review & editing, Data curation. **Paul A. Hooper:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was supported by a CSC Scholarship, the Engineering and Physical Sciences Research Council [grant number EP/X024288/1] and funding from the Department of Mechanical Engineering, Imperial College London.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.matdes.2025.114552>.

Data availability

Data will be made available on request.

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