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Supplementary information

Xolography for linear volumetric 3D printing

In the format provided by the authors and unedited

Peer Review File

Manuscript Title: Xolography for linear volumetric 3D printing

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Ref # 1

After reading this, I believe Xolography is a novel approach for 3D printing. And an exciting one that would be appreciated by the Nature audience. There are a few clarifications that need to be made regarding the specifics of whether this is a true volumetric printing approach, and how appropriate the synthesis is for future scaling of this process.

• Is this actually volumetric as you are printing within a volume, but still layer by layer? It sounds more like a continuous layer by layer printing method within a volume obtaining many of the benefits of volumetric printing including strong surface resolution, no need for supports, and the ability to print enclosed systems like a ball in a cage. True Volumetric Printing should be a 3D printing technique where 3D voxels are cured simultaneously such as the CAL technique (Kelly, et al. 2019) that they reference. The speed at which they print is similar, so it is really only the wording that I'm questioning.

• You don't mention much about the limitations of the resin chemistry itself. With volumetric printing, the optics as well as the chemistry are both highly significant. You discuss the dual-color photo-initiator, but you don't mention the impact of the resin chemistry, the formulations, the viscosity, the transparency, etc. I think this is vital for any paper on a volumetric-like printing approach. The details of the synthesis, in the SI are nice, but please calculate the %yield and include costs. Even if it is low (seems reasonable though from a rough calculation) and expensive, these things improve over time, but it is important for other researchers to gauge their ability to pursue this research.

• How does the 10% beam expansion surrounding the beam waist affect the print? Does it have an impact on the resolution of prints near the edge of the print volume or does it affect how well one beam slice lines up next to the other slice?

• Page 3: You say one-step fabrication, but as you have a linear stage moving the resin vessel continuously, it does not sound like a one-step printing process. At the same time, the CAL method rotates beams. A bit of semantic clarification would be nice, for the philosophical aspect of the work – perhaps in the conclusion, explaining what true volumetric would be – as a goalpost for future research.

• Page 3: "The superposition of expositions leads to a cumulated dose distribution of formed radicals, which solidify cm-sized objects within 30-120 sec and leave other areas below the polymerisation border." This sentence does not sound accurate. I would say "the superposition of expositions leads to a cumulated dose distribution that forms radicals, which solidify cm-sized objects within 30-120 sec and leave other areas below the polymerization limit." I do really like the flow of the first clause though.

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• Page 8: Why are there vertical (y) irradiance variations? Is this an optics issue?

• Page 9: Why would photo-initiators with faster thermal relaxation times impact the print speed if you are moving from one layer to the other? Do you need the latent state from a previous layer to dissipate before exposing the next layer so that you don't have through curing? This would mean that a faster relaxation time would allow you to move from slice to slice faster?

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References:

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footwear production with AM
• 8-15: These are not all layer by layer (2D) printing techniques inherently as some are point-by-point (0D) printing techniques which should be differentiated.

Ref # 2

This is an excellent paper which proposes a novel volumetric 3D printing process. The use of two different wavelengths to activate a chemical reaction (or dual colour) is of great interest. The paper is very well organized and the data supports this new technique. In comparison to the previous techniques, this approach appears to use low light intensity and can build an object in relatively short time with great precision.

1.although this paper reports a new technique, it will be interesting if some mechanical properties could be evaluated. Indeed, it is important to have materials with good mechanical properties. looking the video, the object looks solid and strong.
2. SEM and photo if allows by the journal should have scale bars to indicate the size of the object.
3. the authors mention that the resolution achieved by this technique is 10 times higher. It will be interesting if they can provide a comparison with other techniques. Looking Figure 1, when the light is off, there is a slow decay of the reaction (around 20 s according to the figure), this could reduce the resolution (or make the object less define). this is recognized by the authors by the authors on page 5. The authors mention the half-life is around 6s - it looks a bit short when i look the figure, but it could be a wrong impression.
4. a general review should be added on 3D printing in the introduction. Designing with light: advanced 2D, 3D, and 4D materials Advanced Materials 32 (18), 1903850
5. as the paper takes advantage of the light - perhaps the authors could focus their introduction on the use of light, instead of citing the different AM techniques.
The video are impressive but it takes some time for downloading them. not sure if the authors can reduce the size. In addition, it will be good to show a video in real time just to give the right impression

Ref #3

Summary
The paper presents a volumetric printing method in which a sheet of UV light sensitizes a thin sheet of resin within the volume. A projected image at a second wavelength converts resin to a solid within this sheet, somewhat similar to stereolithography but with no need to add new layers of resin to a moving stage. An obvious challenge, the orthogonal control of polymerization by the two wavelengths, is addressed both by the choice of printer geometry and a calibration process which demonstrates a convincing region where the goals can be met. The chemical and optical engineering details are clearly and fully documented. The paper is well written and I find only minor areas where it could be improved. The concept is novel and will add an interesting new concept to the growing field of volumetric printing techniques.

Specific comments:
1. Depending on the coherence length and path length matching of the two counter-propagating UV beams, there may be a standing wave or other interference patterns (e.g. due to reflections from package boundaries). I doubt this is too significant, but I am curious if you considered this.
2. The images projected at must be in focus at the UV plane which is itself at variable depth within the cuvette. Does the variable thickness of the cuvette (between the surface and the image plane)

impact the quality of the f/2.4 image focus?
3. The phrase "linear parameter space" on page 7 makes little sense until one reads the supplementary information to find that the boundaries of the parameter space are linear in the variable chosen. You might consider phrasing this differently.
4. The authors make a proper comparison of their method to 2-photon polymerization, concluding xolography will be significantly faster. They do not compare with other recent volumetric printing methods mentioned such as CAL. CAL has the inherent challenge that the resin volume must be of low optical density (perhaps a maximum of OD 1) while here the patterning light could theoretically be absorbed strongly within the UV waist of the sensitizing light. However, this assumes that the merocyanine absorption can be very large within the small UV waist. A short analysis of how these two volumetric systems compare at a mechanistic level and the resulting print speed comparison would support the comparison with CAL made in the opening pages.
5. The abstract claims 10x resolution improvement over CAL, however the recent paper from Moser demonstrates 80 micron feature size and here SEM was used to measure "25 µm in the x and y directions and 50 µm in z-direction." The test plate in figure 3 shows that the 10 um bar did not print and the 20 micron bar appears to be shorter and with eroded ends in comparison to the larger bars, indicating radical transport is sufficiently fast at this scale to reduce conversion. How is 10x improvement quoted in the abstract and conclusion justified?

Author Rebuttals to Initial Comments:

Referee #1 (Remarks to the Author):

After reading this, I believe Xolography is a novel approach for 3D printing. And an exciting one that would be appreciated by the Nature audience. There are a few clarifications that need to be made regarding the specifics of whether this is a true volumetric printing approach, and how appropriate the synthesis is for future scaling of this process.

Reply: We thank the reviewer for appreciating the novelty of our approach and for the thoughtful comments about the true nature of our work.

1) Is this actually volumetric as you are printing within a volume, but still layer by layer? It sounds more like a continuous layer by layer printing method within a volume obtaining many of the benefits of volumetric printing including strong surface resolution, no need for supports, and the ability to print enclosed systems like a ball in a cage. True Volumetric Printing should be a 3D printing technique where 3D voxels are cured simultaneously such as the CAL technique (Kelly, et al. 2019) that they reference. The speed at which they print is similar, so it is really only the wording that I'm questioning.

Reply: According to our understanding of volumetric 3D printing, the resin remains static in the vat during the printing process. This is the prerequisite for translating the typically homogeneous structure of the starting material into isotropic properties of the fabricated object. This is in contrast to layer-by-layer 3D printing approaches, in which the volume is moved through deposition or inflow of new material, thereby promoting the creation of inhomogeneities at interfaces to already written structures. As a consequence, support structures are no longer needed and more complex (enclosed) systems can be printed in one step. Volumetric printing can be realized using different projection geometries to address specific locations (voxels) in the volume. In the case of the CAL technique, angular projections are combined with a rotation of the entire circular build volume, while in xolography perpendicular crossing light beams are combined with a linear movement of the entire rectangular build volume. An important aspect relates to the sudden "appearance" of the fabricated object. In both methods, CAL and xolography, radicals are continuously being generated by the absorbed radiation during the writing process. However, while in CAL the polymerization/crosslinking threshold is reached at the end of the writing process connected with an instantaneous appearance of the object based on a nonlinear process, in xolography this process is continuous (linear). Thus, both techniques are truly volumetric printing processes. Inspired by the remark about the idea of simultaneous curing, we have added a new sentence in the discussion and future perspectives section (see comment 4) below.

2) You don't mention much about the limitations of the resin chemistry itself. With volumetric printing, the optics as well as the chemistry are both highly significant. You discuss the dual-color photo-initiator, but you don't mention the impact of the resin chemistry, the formulations, the viscosity, the transparency, etc. I think this is vital for any paper on a volumetric-like printing approach. The details of the synthesis, in the SI are nice, but please calculate the %yield and include costs. Even if it is low (seems reasonable though from a rough calculation) and expensive, these things improve over time, but it is important for other researchers to gauge their ability to pursue this research.

Reply: We fully agree with the reviewer that specific features of the resin have to be tailored to make it suitable for xolography and in fact this is true for any 3D printing method. We have added a new sentence at the end of the section "The Dual Colour Photoinitiator" on page 5: *"The corresponding resins are optimized to provide high chemical reactivity for rapid polymerisation and crosslinking, maximum optical transparency as well as high viscosity."* Moreover, we highlight key features such as optical transparency in the section "printer setup" on page 6 (we added explicitly: *"transparent and"*) and high viscosity in the section "volumetric printing capability" on page 7. The importance of resin development for accessing various types of materials has furthermore been included in the section "Discussion and Future Perspectives" on page 9 by extending a previous sentence to: *"In case of the latter, these could encode for different polymerisation types that in combination with tailored organic, inorganic or cellular resins provide access to a wide variety of (bio)material systems."*

Concerning the synthesis, we have followed the reviewer's advice, calculated the yields and updated the corresponding figure (see new Extended Data Figure 1). Assuming these yields and the price of the starting materials, the cost would amount to approximately 230 Euro per gram of initiator. However, we did not include this price since the synthesis process has not been scaled up and the associated yields have not been optimized (and thus we would expect the number to drop significantly).

3) How does the 10% beam expansion surrounding the beam waist affect the print? Does it have an impact on the resolution of prints near the edge of the print volume or does it affect how well one beam slice lines up next to the other slice?

Reply: Indeed, the beam expansion leads to a minor decrease of resolution along the x-axis (see Figure 1a), which is on the same order as the increase of the light sheet thickness. The other volume directions remain unaffected. As the axis is moved continuously and the projected images stem from digital model slices with a much smaller slice thickness (3.8 µm) than the actual thickness of the light sheet (39 µm waist size), the writing process does not lead to generation of individual slices, so aligning problems do not appear. In general, there is great potential (still unexplored) to manage slight variations and even increase the resolution by viewing the light sheet intensity distribution as an instrument function of the printer that can be accounted for via projected images.

4) Page 3: You say one-step fabrication, but as you have a linear stage moving the resin vessel continuously, it does not sound like a one-step printing process. At the same time, the CAL method rotates beams. A bit of semantic clarification would be nice, for the philosophical aspect of the work – perhaps in the conclusion, explaining what true volumetric would be – as a goalpost for future research.

Reply: This comment addresses two different aspects. The first relates to the "one-step fabrication of complete systems", i.e. without the need to assemble individual parts as briefly explained on page 3 and later eluded to on page 7 by describing "single-step fabrication of parts integrating mechanical functions" and we hope that this is clear. The second one connects to the discussion about point 1) of the same reviewer. Following the considerate comments concerning "true" volumetric printing and the idea of quasi-instantaneous printing (see above), we followed the great advice to summarize the ideal of volumetric printing in the discussion and future perspectives section. There we added the new sentence: "This further development brings us closer to an ideal volumetric method, characterised by a fast, quasi-spontaneous objectification".

5) Page 3: "The superposition of expositions leads to a cumulated dose distribution of formed radicals, which solidify cm-sized objects within 30-120 sec and leave other areas below the polymerisation border." This sentence does not sound accurate. I would say "the superposition of expositions leads to a cumulated dose distribution that forms radicals, which solidify cm-sized objects within 30-120 sec and leave other areas below the polymerization limit." I do really like the flow of the first clause though.

Reply: We changed the sentence following the suggestion.

6) Page 7: Modify this sentence to be…"This feature…mechanical functions; a simple example is the flow cell…"

Reply: We changed the sentence following the suggestion.

7) Page 8: Why are there vertical (y) irradiance variations? Is this an optics issue?

Reply: The laser beam characterized by a small diameter of 1.2 mm (1/e2) is expanded to about 6.5 cm to generate the light sheet. This is associated with a large magnification in the vertical direction. Small deviations from the ideal optical surfaces are thus translated to inhomogeneities in irradiance, as correctly assumed by the reviewer. Currently, we are pursuing various strategies to minimize this effect.

8) Page 9: Why would photo-initiators with faster thermal relaxation times impact the print speed if you are moving from one layer to the other? Do you need the latent state from a previous layer to dissipate before exposing the next layer so that you don't have through curing? This would mean that a faster relaxation time would allow you to move from slice to slice faster?

Reply: Exactly, this is the idea. Faster thermal recovery of the initial dormant spiropyran state would allow for faster printing since previously exposed areas are not sensitive towards visible light any longer.

9) Page 9: Which coordinate limits the size of the print volume? The y-coordinate due to optic *limitations?*

Reply: The size of the print volume is limited in the direction of the light sheet or x-axis only (see Figure 1a). The absorption by the photoinitiator molecules leads to an exponential decrease of the light sheet irradiance while it traverses the volume. We control this effect by irradiating the volume from both opposite sides and thus achieve homogeneous photopolymerization profiles. A theoretical calculation, as presented in the method section, shows that the overlay approach can be used for the current system up to 10 cm volume depth (x). To make this aspect even more clear, we have stated the precise axis in the section "discussion and future perspectives" on page 9.

10) References:

1: Nazir 2019 is a review paper for AM of cellular structures and should not be cited for athletic footwear production with AM

Reply: Obviously, there is no specific publication or review of paper about the cooperation between Adidas and Carbon to mass-produce athletic footwear by 3D printing which we like to reference in the context of quickly expanding AM applications. However, we found it has been discussed recently in a Nature news feature by M. Zastrow "3D printing gets bigger, faster and stronger" *Nature* **578**, 20-23 (2020) and replaced the reference.

11) 8-15: These are not all layer by layer (2D) printing techniques inherently as some are point-by-point (0D) printing techniques which should be differentiated.

Reply: We agree with this valuable comment. Along with response to point 5) by Reviewer #2 we changed the second sentence in the fully referenced summary accordingly. In particular, we focus right away on light-induced AM techniques instead of listing general AM methods. Subsequently, we mention the layer-by-layer as well as the missing point-by-point printing motif in comprehensive form.

Referee #2 (Remarks to the Author):

This is an excellent paper which proposes a novel volumetric 3D printing process. The use of two different wavelengths to activate a chemical reaction (or dual colour) is of great interest. The paper is very well organized and the data supports this new technique. In comparison to the previous techniques, this approach appears to use low light intensity and can build an object in relatively short time with great precision.

Reply: We thank the reviewer for the kind words of appreciation and clearly recognizing the advantages of our method.

1) Although this paper reports a new technique, it will be interesting if some mechanical properties could be evaluated. Indeed, it is important to have materials with good mechanical properties. looking the video, the object looks solid and strong.

Reply: We highly appreciate this comment and have included both qualitative as well as quantitative data on the mechanical properties of the 3D printed materials. On the one hand, we have provided a new supplementary video clearly showing the resilience of a printed object to the impact of a hammer. On the other hand, we have carried out additional measurements, specifically tensile testing and dynamic mechanical analysis (DMA) to determine stress-strain curves and viscoelastic properties, respectively. The mechanical properties are referred to in the main text of the manuscript (on page 8) as well as the method section (on page 21) including the new Extended Data Figure 9.

2) SEM and photo if allows by the journal should have scale bars to indicate the size of the object.

Reply: We apologize for this *faux pas*! Scale bars have been added in all figures.

3) the authors mention that the resolution achieved by this technique is 10 times higher. It will be interesting if they can provide a comparison with other techniques. Looking Figure 1, when the light is off, there is a slow decay of the reaction (around 20 s according to the figure), this could reduce the resolution (or make the object less define). this is recognized by the authors by the authors on page 5. The authors mention the half-life is around 6s - it looks a bit short when i look the figure, but it could be a wrong impression.

Reply: The question concerning the resolution as well as comparing it with known volumetric methods (CAL) has been addressed below in our reply to point 5) of Reviewer #3. Concerning the thermal half-life, we refer to a 50% decay in the absorbance and in fact, the $t_{1/2}$ is 6 sec. The reviewer is right that the thermal half-life influences the printing speed as we refered to above in our reply to Reviewer #1's point 8) and discuss on page 9 of the manuscript (*"It is already foreseeable that the speed will increase significantly utilizing ... photoinitiators with faster thermal relaxation time."*) Interestingly, a decay of less than 50% is already sufficient to go below the polymerization threshold and inhibit hardening, thus leading to faster printing as expected based on the half-life.

4) a general review should be added on 3D printing in the introduction. Designing with light: advanced 2D, 3D, and 4D materials Advanced Materials 32 (18), 1903850

Reply: We moved the mentioned review article from its former last position to seventh place in the list of references and cited the paper as requested in basic-level introduction of the fully referenced summary paragraph.

5) as the paper takes advantage of the light - perhaps the authors could focus their introduction on the use of light, instead of citing the different AM techniques.

Reply: We implemented this suggestion along with the above response to point 11) of Reviewer #1.

6) The video are impressive but it takes some time for downloading them. not sure if the authors can reduce the size. In addition, it will be good to show a video in real time just to give the right impression

Reply: We have reduced the supplementary videos to the essentials and reduced their size.

Referee #3 (Remarks to the Author):

The paper presents a volumetric printing method in which a sheet of UV light sensitizes a thin sheet of resin within the volume. A projected image at a second wavelength converts resin to a solid within this sheet, somewhat similar to stereolithography but with no need to add new layers of resin to a moving stage. An obvious challenge, the orthogonal control of polymerization by the two wavelengths, is addressed both by the choice of printer geometry and a calibration process which demonstrates a convincing region where the goals can be met. The chemical and optical engineering details are clearly and fully documented. The paper is well written and I find only minor areas where it could be improved. The concept is novel and will add an interesting *new concept to the growing field of volumetric printing techniques.*

Reply: We greatly appreciate the reviewer's comments about the originality of our work and its presentation in the manuscript.

1) Depending on the coherence length and path length matching of the two counter-propagating UV beams, there may be a standing wave or other interference patterns (e.g. due to reflections from package boundaries). I doubt this is too significant, but I am curious if you considered this.

Reply: Formerly, we used an interferometric technique to align the superposition of the light sheet in air by detecting interference rings, which show up when the optical path lengths of both arms are equal. Instead, if the counter-propagating light beams travel through the cuvette containing the resin such patterns are not observable due to multiple light scattering reducing coherence.

2) The images projected at must be in focus at the UV plane which is itself at variable depth within the cuvette. Does the variable thickness of the cuvette (between the surface and the image plane) impact the quality of the f/2.4 image focus?

Reply: It is correct that the focus position of projected image shifts with respect to the light sheet plane while the cuvette is moving. Due to the large distance from the projector to the light sheet plane of about 80 cm, the depth of focus was sufficient, thus not affecting the quality of the project image for printing in small volumes. To compensate for this effect, we are implementing a linear stage for the projector, which accompanies our ongoing research efforts to increase the available print volume.

3) The phrase "linear parameter space" on page 7 makes little sense until one reads the supplementary information to find that the boundaries of the parameter space are linear in the variable chosen. You might consider phrasing this differently.

Reply: In response to the proposal, we removed the word linear as it is not necessary to convey the main message, namely a calibration procedure that provides a parameter space of irradiance-velocity pairs for xolography-based 3D printing.

4) The authors make a proper comparison of their method to 2-photon polymerization, concluding xolography will be significantly faster. They do not compare with other recent volumetric printing methods mentioned such as CAL. CAL has the inherent challenge that the resin volume must be of low optical density (perhaps a maximum of OD 1) while here the patterning light could theoretically be absorbed strongly within the UV waist of the sensitizing light. However, this assumes that the merocyanine absorption can be very large within the small UV waist. A short analysis of how these two volumetric systems compare at a mechanistic level and the resulting print speed comparison would support the comparison with CAL made in the opening pages.

Reply: On the mechanistic level, the UV triggered merocyanine absorption is sufficiently strong to allow for efficient dual color curing as the reviewer is suspecting. It is also correct that the patterning light from the projector is only absorbed within the light sheet, thus xolography is capable of processing much larger volumes. In case of xolography, the printing speed depends on the UV dose delivered, defined by the laser irradiance and shifting speed of the vessel. Furthermore, it is affected by the resin composition, namely the type of monomer, concentrations of the photoinitiator and coinitiator. Kelly *et al.* (reference #14) reported a printing speed of 51 sec for an object of about 1 cm diameter and provided an overall range between 30-120 sec as cited on page 3 of our manuscript. This is about the same speed that we publish in the results section of our manuscript on page 7, thus we stated in the first sentence of the summary: *"The volume generation rate as a measure of the printing speed is ... of the same order of magnitude compared to CAL."*

5) The abstract claims 10x resolution improvement over CAL, however the recent paper from Moser demonstrates 80 micron feature size and here SEM was used to measure "25 µm in the x and y directions and 50 µm in z-direction." The test plate in figure 3 shows that the 10 um bar did not print and the 20 micron bar appears to be shorter and with eroded ends in comparison to the larger bars, indicating radical transport is sufficiently fast at this scale to reduce conversion. How is 10x improvement quoted in the abstract and conclusion justified?

Reply: The mentioned paper from Loterie, Delrot & Moser, which we cited and discussed in our manuscript on page 3, reported 80 µm positive features but concurrently a significantly lower value of 500 µm for negative features. Even more important, these values were only achieved by recording the printing process with a camera in a first printing attempt of lower resolution, followed by computational analysis and modification of the angular projections specifically for the desired object to finally print the object a second time, now yielding better results. Obviously, we compare the first pass resolution of xolography to first pass results from CAL, which have been reported to 300 µm resolution in the cited reference #14 from Kelly *et al.* We realized in z-direction a factor of 6 and in x as well as in y direction a 12 times (300 µm/25 µm) higher resolution. In order to state our results more precisely, we replaced the former sentence in the fully referenced paragraph by: *"In reference to state-of-the-art volumetric printing methods, our approach demonstrates without any computational optimisation about ten times higher resolution compared to computed axial lithography…"* The statement in the conclusion has been replaced accordingly.