Web links to the author's journal account have been redacted from the decision letters as indicated to maintain confidentiality.

Decision letter and referee reports: first round

21st Nov 19

Dear Prof Xing,

Thank you for submitting your manuscript, "Nano-Layer Deposition in Liquid Hydrocarbons using Condensed Water Film", to Communications Materials. It has now been seen by 3 referees. You will see from their comments below that while they all find your work of interest, some important points are raised. We are interested in publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a final decision on publication.

Of particular importance is that Referee 1 and 3 are both asking for more discussion of the background literature - to place this study in context - and Referee 1 and 2 ask that limitations of the technique be made clear. I should add that we were not aware that Referee 1 had reviewed the paper previously at Nature Communications (our journals are independent of each other). However, their comments all appear valid to us and we ask that you address them in the revised paper. Referee 2 and 3 also questions the appropriateness of the NLD name. Finally, all the referees ask for some clarifications/additional discussion in the text.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A rebuttal letter with a point-by-point response to each of the referee comments and a description of changes made. Please include the complete referee report in the rebuttal letter. Please note that the rebuttal letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in red colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

-A clean version of the manuscript. Please select the file type 'Article File'.

-An updated Editorial Policy checklist, uploaded as a 'Related Manuscript File' type. This checklist is to ensure your paper complies with all relevant editorial policies. If needed, please revise your manuscript in response to these points. Please note that this form is a dynamic 'smart pdf' and must therefore be downloaded and completed in Adobe Reader, instead of opening it in a web browser.

-Your manuscript should comply with our format requirements, which are summarized on the following checklist:
Communications Materials formatting checklist. Please modify your manuscript according to this checklist.

Please use the following link to submit your revised manuscript files:

[link redacted]

** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to receive your revised paper within three months; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

John Plummer, PhD
Chief Editor
orcid.org/0000-0003-4824-8497
Communications Materials

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The manuscript by Jasim et al. introduces a technique named "NLD" to generate oxide coatings of controllable thickness on suspended nanoparticulate or otherwise powdered solid substrates. This is an interesting novel technique and the experimental data support most of the conclusions very well. However, most of the comments I made in my review for Nature Communications has been implemented, even though most of them would have taken literally less than 10 minutes to implement. Therefore, I recommend rejection.

Here is a summary of my concerns that should have been addressed:
(1) The authors still refuse to acknowledge the existence of methods conceptually and/or experimentally similar to NLD and do not cite the work by Knez and Bae/Shin. The presence of these pieces of work does not in any way restrict the merit of the current authors' method development, but it is required to provide the readers with the full information and as a matter of scientific integrity.
(2) The authors still claim conformality without having tested the coating of concave substrates. Again, the external surfaces of convex structures such as spherical particles and rods or tubes can be coated "conformally" by many methods including sol-gel chemistry. Either the authors present the results on concave structures or they retract the claim of conformal coating.
(3) The authors still avoid mentioning the limitations that their method will likely face with deep pores related to capillary condensation.
(4) The authors still avoid presenting clearly the molar amounts of condensed water, dissolved water, and metal-containing precursor in Tables S1 and S2.
(5) The authors have removed from their conclusions the applications in batteries and plasmonics, for which ALD is arguably better suited, but they do not cite any other application for which NLD would be better suited.
(6) The misleading statement on XRD of alumina has been removed. Now, however, the story has changed: it is no longer supposed to be amorphous Al_2O_3, but crystalline AlOOH.
(7) The reference spectrum taken in the absence of water is still missing.

Reviewer #2 (Remarks to the Author):

This paper describes a new method for the growth of highly conformal metal oxide films on nanoparticles and other nanomaterials, through formation of a uniform nanoscale water layer on the nanomaterials, followed by addition of a metalorganic compound to form the metal oxide layer. This is a highly novel approach, and I am not aware of anything else like it. In this way, oxide

films of Ti, Al, and Nb were created. TEM indicates the formation of completely conformal, uniform thickness oxide layers on the nanomaterials. The authors have made a good case for their new method, and I am sufficiently convinced to be able to support publication. I have numerous comments for the authors to consider in creating a revised manuscript:

1. Since ALD is a hot field, the authors have apparently chosen to use the acronym NLD. This does not feel quite right to me, since the present technique uses only one chemical treatment step and the film thickness is determined by the amount of absorbed water. ALD also requires self-limited reactions, and there is no demonstration herein of self-limited growth. I do not have any alternative names for the new technique, but the authors should think about this issue. Some people in the ALD area may have stronger opinions.

2. I am somewhat concerned about the thickness control that is possible with the new method. Getting exactly the same amount of water in the heptane solution every time may be difficult, and film thicknesses may vary from run to run. Do the authors have any data in this regard?

3. On line 56, it is stated that the organic solvent can be reused. How can the amount of water present in the solvent be controlled? Do the authors assume every time that the solvent is saturated with water? What about excess metalorganic precursors or metal-containing products?

4. Line 61, what is a "measured amount" of TEO? Is this an excess amount, or do the authors calculate how much water is present on the nanomaterials and then add that much TEO? TEO will certainly react with the 61 ppm of water in the solvent, so how do the authors separate growth enabled by hydrolyzed TEO from growth determined by the water layer on the nanomaterials?

5. The authors draw idealized chemical reactions for the formation of metal oxide layers, yet these reactions occur at room temperature. It is highly likely that the oxide layers consist of oxide-hydroxides, which are not the metal oxides presented in the ideal equations. In fact, the authors own data show amorphous films with at least some hydroxide content, e.g. Al(O)OH. The authors should make it very clear that the films are not pure oxides, and are most likely oxide-hydroxides. For example, the statement on line 64 about "amorphous titanium oxides" should be revised so as not to be misleading. The formation of oxide-hydroxides is a potential limitation of the present method.

6. Does the film thickness increase if the author add a large excess of TEO, TMA, etc, for a given water layer thickness? In other words, is there a CVD-like component to the film growth?

7. On line 89, the word "intensively" is inappropriate here. I suggest alternative wording for the beginning of this sentence "The reaction of TMA with water is extremely exothermic, and follows the idealized reaction..."

8. "Conformable" should not be used throughout the paper. Instead, "conformal" should be used.

9. In lines 113-118, the addition of "a small amount of alcohol" to the heptane solutions must change the solubility of water. The authors should comment on this possibility here. Alcohols can also dehydrate, especially in the presence of H+ or Lewis acids.

10. I am slightly concerned that the 99.99% N2 used in the experiments can act as a source of water for the reactions, and that the film thicknesses might be affected. It does not take much water to create films with highly reactive metalorganic compounds.

11. I was somewhat surprised not to see the formation of films on flat substrates reported, such as Si with native oxide. Such films could be studied by IR spectroscopy to probe the presence of OH groups, and also by XPS to assess purity and chemical states.

Reviewer #3 (Remarks to the Author):

This paper reports on a new method to deposit continuous, uniform oxide thin-films conformally

around carbon and oxide nanoparticles and nanotubes. The method cleverly uses the formation of a condensed water layer on the hydrophilic surface in a hydrophobic solvent. I recommend publication of the paper taking into account some of the comments below.

In my opinion, however, the proposed name "Nano-Layer Deposition" does not capture the essence of the new technique. In se, every (uniform or continuous) thin-film can be called a "nano-layer", also those made with Atomic Layer Deposition (ALD), Chemical Solution Deposition (CSD) or electrochemical deposition (ECD), hence, all these techniques are nano-layer deposition techniques, really. A suggestion could be "Condensed Layer Deposition".

The technique holds resemblances to micro-emulsions, reverse micelles and nanoreactors, the difference being that the nanoreactor solution is not inside a micelle in this case but on a surface such an oxide particle or carbon nanostructure. This is indeed a clever adaptation to make thin-film coatings and core-shell particles. However, the authors should make the link to these techniques and provide some background literature.

Does the technique only work with nanostructures? It seems to me this would work in general for any substrate?

Line 28-30: "One commonly used process is the sol-gel technique, in which sols are formed in an aqueous solution and gel when deposited onto a surface to form a thin film" – comment: sol-gel is broader than aqueous gels only. Line 31 "The ALD technique uses water vapor and chemical precursors that can be vaporized." – comment: ALD is not restricted to water vapor either (e.g ozone processes or O2 plasma). If the authors would like to restrict to aqueous or water-based processes (to compare with their condensed water thin-film coating as nanoreactor), then they should build up the argumentation as such.

I understand that oil/water is a characteristic example for hydrophobic/water phase separation systems, but is "heptane" an oil? I guess that in the field of micro-emulsions the terminology "oil phase" is commonly used to indicate the hydrophobic phase in separating mixtures – in which case I suggest the authors introduce these concepts and use of terminology for the reader in the introduction (see also my comment on making the link with micro.

Lines 62-65: "A monomer of TEO reacts with water, according to $Ti(OC2H5)4 + 2H2O = TiO2 + 4C2H5OH$. Incomplete reactions could lead to amorphous titanium oxides, as confirmed from X-ray diffraction (XRD) before and after heat treatment (Supplementary Fig. 2)." Comment: A monomer is used for polymerization but I don't think it applies to the TEO precursor for TiO2 synthesis by hydrolysis reaction. Further, please explain how "incomplete reaction" can lead to amorphous titanium oxides. I know amorphous titanium dioxide but I guess the author refer to impurities, hydroxides,...?

For two surfaces in contact the term typically used (as in ALD literature) is "conformal and conformally; e.g. conformal coating.

Line 235: "mixture of concentrated acid (8.0 M), which consists of 3:1 (v/v) $H2SO4:HNO3$" - comment: is that then an aqueous solution of 6M $H2SO4$ and 2M $HNO3$, or?
Line 264: "SO4 - anions" I assume it should be "SO4 2- anions"

Sentences with grammatical errors:
Line 30: "Another that has been paid much attention is the atomic layer deposition (ALD)"
Line 41: In theory, a wide range of metal oxide nanocoatings can be deposited because a many metalorganic precursors can be dissolved in liquid hydrocarbon.
Line 62: As shown in Fig. 1c and d, titania nanocoatings were clearly see to be deposited on the CNTs.
Line 31 in Suppl. Information

Author rebuttal letter: first round

Manuscript #: COMMSMAT-19-0061
Title: Nano-Layer Deposition in Liquid Hydrocarbons using Condensed Water Film

Responses to Reviewer Comments

The authors appreciate the reviewers' comments. Our responses are given below in blue.

Reviewer #1 (Remarks to the Author):

The manuscript by Jasim et al. introduces a technique named "NLD" to generate oxide coatings of controllable thickness on suspended nanoparticulate or otherwise powdered solid substrates. This is an interesting novel technique and the experimental data support most of the conclusions very well. However, most of the comments I made in my review for Nature Communications has been implemented, even though most of them would have taken literally less than 10 minutes to implement. Therefore, I recommend rejection.

Author response: Thanks for the reviewer's comments in recognizing the novelty of our work. In this revision we did our best to address the reviewer's concerns

Here is a summary of my concerns that should have been addressed:

(1) The authors still refuse to acknowledge the existence of methods conceptually and/or experimentally similar to NLD and do not cite the work by Knez and Bae/Shin. The presence of these pieces of work does not in any way restrict the merit of the current authors' method development, but it is required to provide the readers with the full information and as a matter of scientific integrity.

Author response: We have now cited the following references and added a description of them.

- Seung-Mo Lee, Eckhard Pippel, Ulrich Gösele, Christian Dresbach, Yong Qin, C. Vinod Chandran, Thomas Bräuniger, Gerd Hause, Mato Knez, "Greatly Increased Toughness of Infiltrated Spider Silk". Science 324, 488-492, 2009.
- Itxasne Azpitarte and Mato Knez, "Vapor phase infiltration: from a bioinspired process to technologic application, a prospective review". MRS Commun. 2018, 8, 2018 , 727-741.
- Bae et al., "Rapid, conformal gas-phase formation of silica (SiO2) nanotubes from water condensates". Nanoscale, 2013, 5, 5825.

Obviously these are very good work. These studies all used vapor phase filtration into the pores of a macroscale substrate and used ALD or CVD to react to make a coating inside the pores. However, our work is specifically to coat the outer surfaces of a nanoscale substrate, not the internal pores. We submerse substrates in a liquid hydrocarbon, not in a vapor or gas.

(2) The authors still claim conformality without having tested the coating of concave substrates. Again, the external surfaces of convex structures such as spherical particles and rods or tubes can be coated "conformally" by many methods including sol-gel chemistry. Either the authors present the results on concave structures or they retract the claim of conformal coating.

Author response: Conformality in coating technologies means the coatings follow the shape of the substrate surface, be it on the outside surfaces or inside. We showed that the nanocoatings made from our method followed the shape of outside surface of both spherical particles or elongated fibers, and therefore they are conformal. The results reported in this paper are all about making nanocoatings on the outer

surfaces of a substrate. We did not claim that the technique can make (conformal) coatings inside pores. To make this point clear to readers, we have revised the manuscript to include a specific statement that the work was to make coatings "on the outer surface of nanoscale solid substrates".

(3) The authors still avoid mentioning the limitations that their method will likely face with deep pores related to capillary condensation.

Author response: We would agree with the reviewer, and it's reasonable to assume that there are limitations to coat inside pores due to capillary effect. But again, as stated above, this work is all about making nanocoatings on the outside surfaces of nanoscale substrates. It's not that we "avoid" mentioning limitations in coating deep pores. We have not studied that, and therefore could not provide a conclusion on that.

In coating carbon nanotubes, we did not see coatings inside. This could be due to (1) capillary effect that the water cannot get inside the nanotubes, (2) the nanotubes are made from CVD and the ends of the nanotubes are closed (sometimes blocked by the catalyst particles); many of them seems to have bamboo structures with no all-through channels.

(4) The authors still avoid presenting clearly the molar amounts of condensed water, dissolved water, and metal-containing precursor in Tables S1 and S2.

Author response: The (actual) added water amount in volume has been given in the Tables. The molar amount is a simple conversion from the volume. For example, a 1 micro-liter water at 20 °C is equivalent to 55.40 micro moles. The dissolved water was also given, which is related to the solvent used. For heptane, it's 61 ppm by volume at 20 °C (see Supplementary Fig. 1).

(5) The authors have removed from their conclusions the applications in batteries and plasmonics, for which ALD is arguably better suited, but they do not cite any other application for which NLD would be better suited.

Author response: We deleted those presumed examples because we tried not to give guesses, but only presented what were demonstrated.

(6) The misleading statement on XRD of alumina has been removed. Now, however, the story has changed: it is no longer supposed to be amorphous Al2O3, but crystalline AlOOH.

Author response: In our previous submission we stated that due to overlaps of diffraction peaks we could not decide whether the alumina is amorphous or crystalline in that specific sample. But we also provided evidence later in that manuscript that the alumina was crystalline bohmite due to no overlaps in that sample. In this submission, we actually accepted the reviewer's previous comment saying that our original statement is "nonsensical or even misleading". We now only reported what can be concluded. So the story has not changed.

(7) The reference spectrum taken in the absence of water is still missing.

Author response: The fact that there is a nanolayer already seen in the TEM images can attest the existence of ice. A bare substrate absence of water would not show any nanolayer (see Fig. 1b, 1f). The EELS result is specifically characteristic of oxygen in ice, which is just additional proof.

Reviewer #2 (Remarks to the Author):

This paper describes a new method for the growth of highly conformal metal oxide films on nanoparticles and other nanomaterials, through formation of a uniform nanoscale water layer on the nanomaterials, followed by addition of a metalorganic compound to form the metal oxide layer. This is a highly novel approach, and I am not aware of anything else like it. In this way, oxide films of Ti, Al, and Nb were created. TEM indicates the formation of completely conformal, uniform thickness oxide layers on the nanomaterials. The authors have made a good case for their new method, and I am sufficiently convinced to be able to support publication. I have numerous comments for the authors to consider in creating a revised manuscript:

Author response: Thanks for the reviewer's comments in recognizing the novelty of our work.

1. Since ALD is a hot field, the authors have apparently chosen to use the acronym NLD. This does not feel quite right to me, since the present technique uses only one chemical treatment step and the film thickness is determined by the amount of absorbed water. ALD also requires self-limited reactions, and there is no demonstration herein of self-limited growth. I do not have any alternative names for the new technique, but the authors should think about this issue. Some people in the ALD area may have stronger opinions.

Author response: We appreciate this advice. We have now changed it to "Condensed Layer Deposition" or CLD as an acronym.

2. I am somewhat concerned about the thickness control that is possible with the new method. Getting exactly the same amount of water in the heptane solution every time may be difficult, and film thicknesses may vary from run to run. Do the authors have any data in this regard?

Author response: We thank the reviewer's comment. Based on the experimental results, the thickness can be well controlled. For example, to make 5-nm the results based on the TEM are within the range of (4-7 nm). The deviations are attributed to the experimental error from using a syringe to add the water. Such errors could be further reduced if further precise control can be achieved.

3. On line 56, it is stated that the organic solvent can be reused. How can the amount of water present in the solvent be controlled? Do the authors assume every time that the solvent is saturated with water? What about excess metalorganic precursors or metal-containing products?

Author response: After the coating experiment is done, the nanomaterial-heptane mixture is centrifuged. The separated heptane is poured in a big container (2 L) each time until it is almost full. Then we over saturate this container by water to react with any left-over metalorganic precursors or metal-containing products under severe stirring. A white powder is seen to precipitate at the bottom. After settling overnight, the heptane is collected from the top. It is then filtered by 0.45 micron filter to remove any particles. When we use the recovered and purified heptane, we barely see any contamination from previous chemistry. We would note that for more accuracy, the heptane can be purified by distillation.

Heptane is in thermodynamic equilibrium with water (see Fig. S1), so the dissolved water in heptane is fixed at a fixed temperature, if given time for reaching equilibrium. We have updated the content in line 56 in the revised manuscript.

4. Line 61, what is a "measured amount" of TEO? Is this an excess amount, or do the authors calculate how much water is present on the nanomaterials and then add that much TEO? TEO will certainly react

with the 61 ppm of water in the solvent, so how do the authors separate growth enabled by hydrolyzed TEO from growth determined by the water layer on the nanomaterials?

Author response: The “measured amount of TEO” is based on the added water with a little excess taking into account of the 61 ppm.

As the reviewer rightly thought so, when the metal precursor is added, it would also react with the dissolved water in the heptane. While more research needs to be done to elucidate this, we believe that since the water is dissolved in heptane, the reaction will lead to the formation of molecular metal oxides. Even though they do not form on the substrates, the substrates (in high concentration) will act as a scavenger, and given enough diffusion time, the molecular metal oxides would be very much incorporated into the nanocoatings. Since their size is small (even if they form dimers, trimers, etc.) as compared to the nanocoating formed, they cannot be distinguished at this time. The amount of the molecular oxides is not significant (<3%), especially when the coatings are thick (>10 nm).

5. The authors draw idealized chemical reactions for the formation of metal oxide layers, yet these reactions occur at room temperature. It is highly likely that the oxide layers consist of oxide-hydroxides, which are not the metal oxides presented in the ideal equations. In fact, the authors own data show amorphous films with at least some hydroxide content, e.g. Al(O)OH. The authors should make it very clear that the films are not pure oxides, and are most likely oxide-hydroxides. For example, the statement on line 64 about "amorphous titanium oxides" should be revised so as not to be misleading. The formation of oxide-hydroxides is a potential limitation of the present method.

Author response: We thank the reviewer for the comment. Generally, ethoxides are expected to produce metal hydroxide in amorphous phase, taking in account that we did the work at room temperature. However, the TMA produces Al(O)OH (boehmite) - gamma phase, which is still a metal hydroxide but dehydrated and is crystalline. This is because of the heat released from the TMA/ water reaction. The heat helps dehydrate the initially-produced aluminum hydroxides.

We agree with the reviewer and revised some statements to include hydroxides to avoid misleading in this regard.

6. Does the film thickness increase if the author add a large excess of TEO, TMA, etc, for a given water layer thickness? In other words, is there a CVD-like component to the film growth?

Author response: We do not believe there was a CVD growth process. This was also confirmed during purification of used heptane when extra water was added, which immediately produced metal oxide colloids as observed. This means the extra metal organic precursor was still in the heptane unreacted and did not go through a CVD process, at least not significantly. More studies may be needed to further confirm this.

7. On line 89, the word "intensively" is inappropriate here. I suggest alternative wording for the beginning of this sentence "The reaction of TMA with water is extremely exothermic, and follows the idealized reaction..."

Author response: We thank the reviewer’s comment. Correction has been placed in the revised manuscript.

8. "Conformable" should not be used throughout the paper. Instead, "conformal" should be used.

Author response: Thank you for the correction. It has been replaced in the revised manuscript.

9. In lines 113-118, the addition of "a small amount of alcohol" to the heptane solutions must change the solubility of water. The authors should comment on this possibility here. Alcohols can also dehydrate, especially in the presence of H+ or Lewis acids.

Author response: We thank the reviewer for the comment. The ethanol addition might change the solubility of water, for which we have not studied. However, we added the ethanol after the water addition and condensation, which means that the ethanol has to first diffuse to the substrate surface to induce any changes. Since ethanol mixes with water through the hydroxyl tails, and the ethyl side would be exposed to heptane, it would be difficult for water to diffuse out and change its solubility. Nevertheless, this is a good point and could be a study going forward.

As far as dehydration, we think it's less likely at the time it mixes with water that is pure. During the reaction process, it could occur due to hydrolysis reactions. However, we note that dehydration catalyzed by Lewis acids often needs a much higher temperature.

10. I am slightly concerned that the 99.99% N2 used in the experiments can act as a source of water for the reactions, and that the film thicknesses might be affected. It does not take much water to create films with highly reactive metalorganic compounds.

Author response: The nitrogen is a protection gas. It was flowing very slowly. In addition, the moisture level in the ultrahigh purity nitrogen is even lower than the solubility of water in the heptane.

11. I was somewhat surprised not to see the formation of films on flat substrates reported, such as Si with native oxide. Such films could be studied by IR spectroscopy to probe the presence of OH groups, and also by XPS to assess purity and chemical states.

Author response: This work is solely focused on making coatings on nanomaterials. We will report more results in the future.

Reviewer #3 (Remarks to the Author):

This paper reports on a new method to deposit continuous, uniform oxide thin-films conformally around carbon and oxide nanoparticles and nanotubes. The method cleverly uses the formation of a condensed water layer on the hydrophilic surface in a hydrophobic solvent. I recommend publication of the paper taking into account some of the comments below.

Author response: We thank the reviewer for reviewing the manuscript.

In my opinion, however, the proposed name "Nano-Layer Deposition" does not capture the essence of the new technique. In se, every (uniform or continuous) thin-film can be called a "nano-layer", also those made with Atomic Layer Deposition (ALD), Chemical Solution Deposition (CSD) or electrochemical deposition (ECD), hence, all these techniques are nano-layer deposition techniques, really. A suggestion could be "Condensed Layer Deposition".

Author response: We appreciate very much the reviewer's suggestion. We now change it to "Condensed Layer Deposition" or CLD.

The technique holds resemblances to micro-emulsions, reverse micelles and nanoreactors, the difference being that the nanoreactor solution is not inside a micelle in this case but on a surface such an oxide particle or carbon nanostructure. This is indeed a clever adaptation to make thin-film coatings and core-shell particles. However, the authors should make the link to these techniques and provide some background literature.

Author response: We appreciate this comment. We have made a link of these topics in the introduction in the revised manuscript. The reverse micelles and nano/micro emulsion principles have been addressed.

Does the technique only work with nanostructures? It seems to me this would work in general for any substrate?

Author response: This work is solely focused on making coatings on nanomaterials. We also believe it should be applied to other substrates. As a matter of fact, we have made coatings on micron-sized powder substrates.

Line 28-30: "One commonly used process is the sol-gel technique, in which sols are formed in an aqueous solution and gel when deposited onto a surface to form a thin film" – comment: sol-gel is broader than aqueous gels only. Line 31 "The ALD technique uses water vapor and chemical precursors that can be vaporized." – comment: ALD is not restricted to water vapor either (e.g ozone processes or O2 plasma). If the authors would like to restrict to aqueous or water-based processes (to compare with their condensed water thin-film coating as nanoreactor), then they should build up the argumentation as such.

Author response: We have revised our statements to limit the scope to avoid misleading.

I understand that oil/water is a characteristic example for hydrophobic/water phase separation systems, but is "heptane" an oil? I guess that in the field of micro-emulsions the terminology "oil phase" is commonly used to indicate the hydrophobic phase in separating mixtures – in which case I suggest the authors introduce these concepts and use of terminology for the reader in the introduction (see also my comment on making the link with micro.

Author response: We have given statements related to micro-emulsions, so the terminology would not mislead the readers.

Lines 62-65: “A monomer of TEO reacts with water, according to $Ti(OC_2H_5)_4 + 2H_2O = TiO_2 + 4C_2H_5OH$. Incomplete reactions could lead to amorphous titanium oxides, as confirmed from X-ray diffraction (XRD) before and after heat treatment (Supplementary Fig. 2).” Comment: A monomer is used for polymerization but I don’t think it applies to the TEO precursor for TiO_2 synthesis by hydrolysis reaction. Further, please explain how “incomplete reaction” can lead to amorphous titanium oxides. I know amorphous titanium dioxide but I guess the author refer to impurities, hydroxides,...?

Author Response:

We have changed the “monomer” to “molecule”.

Ethoxides are expected to hydrolyze to produce metal hydroxide in amorphous phase, taking into account that we did the work at room temperature. However, the TMA produces gamma-Al(O)OH (boehmite), which is a metal oxide-hydroxide, or partially dehydrated form of hydroxide, with a crystalline phase. This latter was attributed to that the high exothermic heat release from the reaction helps dehydration. We have revised some statements to avoid misleading in this regard.

For two surfaces in contact the term typically used (as in ALD literature) is “conformal and conformally; e.g. conformal coating.

Author response: We agree with the reviewer and the term was changed.

Line 235: “mixture of concentrated acid (8.0 M), which consists of 3:1 (v/v) H_2SO_4:HNO_3” - comment: is that then an aqueous solution of 6M H_2SO_4 and 2M HNO_3, or?

Line 264: “SO_4 - anions” I assume it should be “SO_4 2- anions”

Author response: Both acids have an equal concentration which is 8.0 M aqueous solution. The 3:1 (v/v) means the amount of the sulfuric acid is 3 and that of nitric acid is 1.

Yes, it is SO_4^{2-} anions. It has been updated.

Sentences with grammatical errors:

Line 30: “Another that has been paid much attention is the atomic layer deposition (ALD)”

Line 41: In theory, a wide range of metal oxide nanocoatings can be deposited because a

many metalorganic precursors can be dissolved in liquid hydrocarbon.

Line 62: As shown in Fig. 1c and d, titania nanocoatings were clearly see to be deposited on the CNTs.

Line 31 in Suppl. Information

Author response: All four are now addressed in the revised manuscript.

Decision letter and referee reports: second round

15th Dec 19

Dear Prof Xing,

Thank you for submitting your revised manuscript, "Nano-Layer Deposition in Liquid Hydrocarbons using Condensed Water Film", to Communications Materials. It has now been seen again by the 3 referees, whose comments are all appended below. While Reviewer 2 and 3 are mostly happy with the revisions, Reviewer 1 does not feel that their concerns have been addressed. We would in principle be happy to publish your paper, but we will not be able to accept it until the reasonable requests that Reviewer 1 has made are completed.

Reviewer 1 is asking for the following:
- A full discussion of how the method reported here compares to previous works. We would expect at least one full paragraph on this point.
- If coatings on concave samples are not shown then "conformal" must be removed throughout the text. Likewise, discussion should be added as to whether or not this method is applicable for porous or concave substrates.
- Lastly, they ask that details be added regarding stoichiometry of water and reagents, and an EELS spectra in the absence of water.

None of these requests seem too substantial to us, but are important for placing the work in the appropriate context. If you have any concerns regarding these requests, or would like further clarity, then please do not hesitate in messaging me (john.plummer@nature.com).

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised. When submitting your revised manuscript, please include the following:

-A rebuttal letter with a point-by-point response to each of the referee comments and a description of changes made. Please include the complete referee report in the rebuttal letter. Please note that the rebuttal letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in red colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

-A clean version of the manuscript. Please select the file type 'Article File'.

-An updated Editorial Policy checklist, uploaded as a 'Related Manuscript File' type. This checklist is to ensure your paper complies with all relevant editorial policies. If needed, please revise your manuscript in response to these points. Please note that this form is a dynamic 'smart pdf' and must therefore be downloaded and completed in Adobe Reader, instead of opening it in a web browser.

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Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

John Plummer, PhD
Chief Editor
orcid.org/0000-0003-4824-8497
Communications Materials

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The authors have started to implement changes to their manuscript as suggested, however with the least possible acknowledgement of the existing literature and the limitations of the method, or even slightly below the bare minimum that could be considered good scientific practice. I repeat my statement that their method is elegant and worthy of publication, but that I consider it against the standards of scientific publishing to oversell it and refuse to describe openly how the novel method is related to previous work by other authors, or what limitations this method has for practical applications. In that respect, I consider the manuscript in its current form still unfit for publication.

-- (To my comment 1) The three papers that I suggested to cite on similar pieces of work have been added (references 7-9) but without mentioning the relationship to the current method. The sentence "Another method using gas infiltration has been reported to make coatings, especially on internal surfaces or pores" is nondescriptive and must be replaced by a proper presentation at the end of the introduction. Something such as "The CLD method can be considered as a generalization of previously published work such as ...." might be adequate.

-- (To my comment 2) If the authors refuse to show coatings on concave surfaces, they have to remove the word "conformal" from their text. This word is specifically used to describe coatings inside pores, see for example the following very recent review: Appl. Phys. Rev.6, 021302 (2019); doi: 10.1063/1.5060967. The coating of convex substrates such as spherical particles and the outer surface of CNTs is not extraordinary and can be achieved by sel-gel chemistry, as well.

-- (To my comment 3) The authors still refuse to describe in the manuscript that their method is not applicable to porous or otherwise concave substrates.

-- (To my comment 4) Please, please, do provide a comparison of molar amounts of water and co-reagents in the tables in SI. The reader would like to know in what stoichiometric amounts the two reagents are present. Comments 3, 4 and 6 by Reviewer 2 show that I am not the only one interested in stoichiometry and molar amounts.

-- (To my comment 7) The EELS spectrum taken in the absence of water (reference spectrum for Figure 2c) must be provided. In its absence, the presence of oxygen in EELS could simply be due to defective CNTs (which feature oxygenated surface groups).

Reviewer #2 (Remarks to the Author):

The authors have addressed almost all of my comments and concerns in this revision. One issue remains: the authors wording with titania and niobia suggest to the reader that the author have formed pure TiO2 and Nb2O5 under the synthesis conditions. I am not convinced (from the authors' data) that this is the case. It is possible and even likely that there are Ti-OH and Nb-OH bonds in the materials deposited by the synthesis method. These OH groups would then dehydrate upon thermolysis to afford TiO2 and Nb2O5. The authors clearly present the formation of Al(O)OH and not Al2O3.

If the wording associated with the titanium and niobium coatings is resolved, then I support publication.

Reviewer #3 (Remarks to the Author):

The questions and comments have been fully addressed by the authors and the paper is ready for publication.

Author rebuttal letter: second round

Manuscript #: COMMSMAT-19-0061A

Title: Nano-Layer Deposition in Liquid Hydrocarbons using Condensed Water Film

Responses to Reviewer Comments

The authors would like to thank the reviewers for their reviews. We have tired our best to address the reviewers' concerns, which are given below in blue color.

Reviewer #1 (Remarks to the Author):

The authors have started to implement changes to their manuscript as suggested, however with the least possible acknowledgement of the existing literature and the limitations of the method, or even slightly below the bare minimum that could be considered good scientific practice. I repeat my statement that their method is elegant and worthy of publication, but that I consider it against the standards of scientific publishing to oversell it and refuse to describe openly how the novel method is related to previous work by other authors, or what limitations this method has for practical applications. In that respect, I consider the manuscript in its current form still unfit for publication.

Author response: Thanks for the comments. We have tired to address all the concerns in the new revision.

-- (To my comment 1) The three papers that I suggested to cite on similar pieces of work have been added (references 7-9) but without mentioning the relationship to the current method. The sentence "Another method using gas infiltration has been reported to make coatings, especially on internal surfaces or pores" is nondescriptive and must be replaced by a proper presentation at the end of the introduction. Something such as "The CLD method can be considered as a generalization of previously published work such as ...." might be adequate.

Author response: We appreciate the constructive comment. We have now expanded the introduction section. In particular, we have connected our work with the gas infiltration using condensates and microemulsions with water in oil droplets, and acknowledged that our work is "built on the above work".

-- (To my comment 2) If the authors refuse to show coatings on concave surfaces, they have to remove the word "conformal" from their text. This word is specifically used to describe coatings inside pores, see for example the following very recent review: Appl. Phys. Rev.6, 021302 (2019); doi: 10.1063/1.5060967. The coating of convex substrates such as spherical particles and the outer surface of CNTs is not extraordinary and can be achieved by sel-gel chemistry, as well.

Author response: Our results demonstrated that coatings are made at the neck regions of the nanoparticles (in Fig. 4c, SI Fig. 3,4, and 5), where it is a concave surface (see below illustration). It is an indication that the technique can coat concave surfaces. We would like to note that coatings are called

"conformal" in previous publications when they are on the outside surfaces (see for example, DOI: 10.1002/cphc.201000158: Riley, L.A., Cavanagh, A.S., George, S.M., Jung, Y.S., Yan, Y., Lee, S.H. and Dillon, A.C., 2010. Conformal Surface Coatings to Enable High Volume Expansion Li - Ion Anode Materials. ChemPhysChem, 11(10), pp.2124-2130.).

To address the reviewer's concern, we now make a clearly specific statement in the revised manuscript that "While the CLD technique is able to coat the neck region where the surface is concave, it may not be able to make a conformal coating inside nanochannels that was achieved in the gas filtration method" (page 12, Discussion section). This is on top of previous statement to define our work to make coating "on the outer surface of nanoscale solid substrates".

-- (To my comment 3) The authors still refuse to describe in the manuscript that their method is not applicable to porous or otherwise concave substrates.

Author response: As mentioned above, we have specifically made a statement in the revised manuscript that our technique may not make a conformal coating in the inside pores.

-- (To my comment 4) Please, please, do provide a comparison of molar amounts of water and co-reagents in the tables in SI. The reader would like to know in what stoichiometric amounts the two reagents are present. Comments 3, 4 and 6 by Reviewer 2 show that I am not the only one interested in stoichiometry and molar amounts.

Author response: The molar amounts of water and stochiometric molar amounts of precursor reagents are added in the tables in SI, together with the actually used amounts of the precursor reagents.

-- (To my comment 7) The EELS spectrum taken in the absence of water (reference spectrum for Figure 2c) must be provided. In its absence, the presence of oxygen in EELS could simply be due to defective CNTs (which feature oxygenated surface groups).

Author response: We now have done the measurements and this new result is added in the supplementary information as Fig. 9.

Reviewer #2 (Remarks to the Author):

The authors have addressed almost all of my comments and concerns in this revision. One issue remains: the authors wording with titania and niobia suggest to the reader that the author have formed pure TiO2 and Nb2O5 under the synthesis conditions. I am not convinced (from the authors' data) that this is the case. It is possible and even likely that there are Ti-OH and Nb-OH bonds in the materials deposited by the synthesis method. These OH groups would then dehydrate upon thermolysis to afford TiO2 and Nb2O5. The authors clearly present the formation of Al(O)OH and not Al2O3.

If the wording associated with the titanium and niobium coatings is resolved, then I support publication.

Author response: Thanks for the comments. We have addressed this by specifically stating the "titania" and "niobia" contain hydroxides in the revised paper (page 12, Discussion section).

Reviewer #3 (Remarks to the Author):

The questions and comments have been fully addressed by the authors and the paper is ready for publication.

Author response: I appreciate the reviewer's evaluation.

Decision letter and referee reports: third round
20th Jan 20

Dear Prof Xing,

Your manuscript titled "Nano-Layer Deposition in Liquid Hydrocarbons using Condensed Water Film" has now been seen again by Referee 1, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work.

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* Please consider the below title and abstract, which have been slightly edited for clarity (please update the title of Supplementary Information accordingly):

Title: Nano-layer deposition of metal oxides via a condensed water film

Abstract: Nanocoatings on solids can be achieved by various processes, including sol-gel and atomic layer deposition. [SUGGEST ADDING ONE SENTENCE HERE ABOUT WHY NEW PROCESSES ARE NEEDED] Here, we report a versatile and fundamentally different technique, termed condensed layer deposition, for depositing conformal metal oxide nanocoatings on nanoparticles and nanofibers. This approach involves water in liquid hydrocarbons condensing as a nanoscale water film on the substrate surface, enabled by interfacial tension between polar water and nonpolar liquid hydrocarbons. Chemical precursors are then added, which react with the condensed water film to form a metal oxide nanocoating. We demonstrate this for titania, alumina, and niobia on substrates including carbon nanotubes, iron oxide particles and carbon black. Condensed layer deposition can achieve oxide nanocoatings on a variety of substrates with tunable thickness, in one pass, at room temperature.

* We suggest amending the sub-section titles in the results to the following:
Nanocoating by condensed layer deposition
Water film formation and nanocoating thickness
Nanocoating conformality and despoited nanostructures

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If a community resource is unavailable, data can be submitted to generalist repositories such as figshare or Dryad Digital Repository. Please provide a unique identifier for the data (for example a DOI or a permanent URL) in the data availability statement, if possible. If the repository does not provide identifiers, we encourage authors to supply the search terms that will return the data. For data that have been obtained from publically available sources, please provide a URL and the specific data product name in the data availability statement. Data with a DOI should be further cited in the methods reference section.

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"Nano-scale coatings are important for controlling the functional behavior of surfaces. Here, a deposition process is reported for metal oxides, in which a thin water coating on the substrate reacts with chemical precursors, forming a nano-scale layer."

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* The final version of your text as a Word or TeX/LaTeX file, with any tables prepared using the Table menu in Word or the table environment in TeX/LaTeX and using the 'track changes' feature in Word.

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* An updated Editorial Policy checklist, uploaded as a ‘Related Manuscript File’ type. This checklist is to ensure your paper complies with all relevant editorial policies. Please note that this form is a dynamic ‘smart pdf’ and must therefore be downloaded and completed in Adobe Reader, instead of opening it in a web browser.

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Best regards,

John Plummer, PhD
Chief Editor
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REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

The referee comments have now been addressed adequately and the manuscript can be published.