nature portfolio

Peer Review File

Bridged emulsion gels from polymer–nanoparticle enabling large-amount biomedical encapsulation and functionalization

Corresponding Author: Professor Caili Huang

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
Emulsion gels with a network of droplets play an important role in fields of cosmetics, foods and drugs, due to their ability on large-amount encapsulation and on-demand delivery. The manuscript by Wan et al. describes a simple, effective interfacial engineering approach, which utilizes a polymer to precisely program the interfacial assembly of nanoparticles, achieving emulsion gels bridged by facet-shared nanoparticle monolayers. The approach avoids complicated steps of emulsification, gelation and surface modifications of NPs. The system is versatile, where a wide library of chemistries is accessible in the formation of emulsion gels, facilitating their applications. Based on this, the authors prepare a sunscreen for skin protection. Encapsulated bioactive ingredients show better performances than commercial products.

The results are interesting. The interfacial 45° three-phase contact angle of polymer-tailored nanoparticles is suggested to be an important parameter in the formation of bridged emulsion gels than the well-defined surface chemistry of nanoparticles. The studies reveal important fundamental aspects of the emulsion gel formation. The results open up new avenues for the synthesis of next-generation emulsion gel materials from the structured soft templates. The experiments are done carefully, and the presentation is clear. The manuscript is recommended for publication in Nature Communications. Some minor comments are suggested below.

1. In Figure 1a, why does the addition of nanoparticles to the aqueous solution (0.5% w/w) result in a reduction in γ (~ 34.5 mN m–1) as compared to that between pure water and toluene (~ 36 mN m–1)?
2. Some related papers on interfaces are suggested, such as Chin. Chem. Lett. 2022, 33, 3973 and Chin. Chem. Lett. 2023, 34, 107738.
3. How is the stability of the emulsion gels? Will it be stable below zero degree? Will it be stable against high-speed centrifugation?
4. Will the addition of drugs influence the stability of the emulsion gels?
5. The format should be consistent throughout the manuscript. For example, MW = 1,000 g mol–1”.
6. There are some typos, for example, “PDSM-NH2”.

Reviewer #2

(Remarks to the Author)
Remarks to the Author:
In this manuscript, the authors reported a simple strategy utilizing a polymer (PDMS-NH2) to modulate the assembly of nanoparticles (NPs) at the water/oil interface. This approach obtained a 45° three-phase contact angle for the nanoparticles, which allowed them to cross the interface of the oil emulsion and eventually form an interconnected macroscopic network. Their bridging backbone and rheological properties could be tuned over a wide range. This method of assembly was simple and efficient and could be widely used in different biomedical scenarios. However, there are still some problems as follows before published:
1. The scale of the fluorescence images in Fig. 2 should be kept consistent, as in the localized magnification in Fig. 2a (i) as well as in Fig. 2b (ii). In addition, Fig. 2b (ii) also needs to be provided with a localized magnification for consistency.
2. Supplementary Fig. 10 Whether the 3:7 scale localized magnified confocal microscopy results provide a clearer picture.
3. The encapsulation rate and loading capacity of emulsion gels as a carrier form for model bioactive molecules are two

important metrics when applied. Please add relevant experiments.
4. Due to the extremely wide range of biomedical applications and higher requirements for emulsion gel stability in different environments, please supplement the pH stability and ion concentration stability experiments of emulsion gels.
5. In this study, β-carotene was chosen as a model bioactive molecule. However, there is not enough research content on the stability of β-carotene related to its use to protect the skin from UV irradiation damage. Please add experiments related to UV stability and thermal stability of emulsion gels encapsulating β-carotene.
6. UV shielding rate measurement is also an important test for emulsion gel systems used for skin UV protection.
7. Prior to animal experiments, please add relevant in vitro cytological evaluations:
Cytotoxicity testing of emulsion gels.
Emulsion gel for keratin-forming cell protection and inhibition of UV-induced ROS production.
Effect of emulsion gels on mitochondrial membrane depolarization.
8. The following experiments and indicators still need to be added to the animal model of protecting the skin from UV radiation damage:
Relative melanin and relative erythema values for each group of mice at the end of UV treatment.
Relative epidermal thickness and relative keratin percentage in each group of mice at the end of UV treatment.

Reviewer #3

(Remarks to the Author)
The manuscript NCOMMS-24-27831 by Wan et al. introduces a facile method for the synthesis of particulate emulsion gels through polymer-mediated interfacial assembly of nanoparticles. While this mechanism of emulsion stabilization is not novel [R1], its implementation for the synthesis of particulate emulsion gels can be considered so. The authors extensively characterised the synthesized particulate emulsion gels with a variety of complimentary experimental techniques suitable for the material (e.g. confocal microscopy, oscillatory rheology). Through an interdisciplinary approach, the authors additionally provide an interesting proof-of-concept through the encapsulation and subsequent release of sunscreen ingredients in the synthesized particulate emulsion gels. However, I believe the claim of achieving specifically a bridged emulsion gel over the entire presented experimental range is not sufficiently substantiated. If this issue is addressed (vide infra), I would consider this manuscript suitable for publication in Nature Communications.

Following is a more detailed discussion on the points described above, in addition to recommendations on how to potentially address the mentioned issues.

The manuscript contains two distinct claims. The first is the facile synthesis of a particulate emulsion gel, brought about by polymer-regulated interfacial assembly of nanoparticles. The second is that, over a wide range of experimental conditions, the emulsion droplets are connected through nanoparticle bridges consisting of only a single monolayer. I believe it warranted to address both of these claims separately.

The work presented in the manuscript fully supports the first claim. The combination of confocal microscopy and oscillatory rheology makes it abundantly clear that emulsion particulate gels have been formed over a wide range of experimental conditions, simply through shearing the loaded oil and water phases. While the proposed mechanism of emulsion droplet stabilization through nanoparticle/polymer assemblies is not novel [R1] , its application for the synthesis of particulate emulsion gels could be considered so. Additionally, the manuscripts provides a very interesting proof-of-concept through the encapsulation and subsequent release of some of the active compounds of sunscreen . As it is outside by expertise I will refrain from making comments on the histological analysis shown in the manuscript, but the concept looks promising.

My main concerns, however, lie with the second claim. In my opinion, the work presented in the manuscript does not sufficiently substantiate the claim that the emulsion droplets are bridged through nanoparticle monolayers over the entire range of experimental conditions.
In particular, there appear to be consistent differences between experimental findings for the emulsion particulate gels with less than 2wt% nanoparticles in the aqueous phase compared to those with higher nanoparticle content. For example, whereas the confocal image in Figure 2a shows that the oil droplets in the polymer/NP ensemble with 2 wt% nanoparticles display the distinct, polygonal shape associated with bridging [R2], this is notably much less the case for the other confocal images (with higher NP content) in Figure 2 and Figure 1c. Additionally, Figure 3e gives the impression of two distinct scaling regimes for the zero-shear storage modulus and yield stress in the low and high regions of nanoparticle weight fraction, where the latter one has a higher power-law exponent compared to the former (indicating different droplet-droplet interaction). While I agree with the authors that the described power-law behaviour of the highlights the uniqueness of the system compared to others [R2], I do not believe it unambiguously supports the notion of continuous droplet bridging over the presented experimental range.

Another issue for the claim of bridged emulsion droplets is that the extrapolate findings from systems with much larger, nicely spherical nanoparticles (diameter 630 nm) to systems made with the much smaller, commercial Ludox HS-40 nanoparticles (diameter 12 nm). While droplet bridging has been extensively studied for particles in the former size-range, this is not the case for the latter. In particular, for the smaller Ludox particles the exact value of the contact angle (along with pH and ionic strength) is expected to play a much more crucial role in their ability to form bridges between emulsion droplets [R3]. In that regard, I find it unlikely that the found 45 degree contact angle for the large nanoparticles can be directly transposed on the smaller Ludox nanoparticles, in addition to this value being maintained over the relatively broad range of polymer concentrations described in the manuscript.

Finally, I would like to provide some options to the authors for addressing my concerns with regards to the second claim. The first is to just unambiguously show the monolayer bridging of emulsion droplets for polymer/NP ensembles with higher than 2 wt% nanoparticles. A potential way to directly show this is through analysis of the Gaussian curvature of the particle surfaces in the emulsion gels [R2]. An alternative (and perhaps easier) method is to compare the presented results with those from particulate emulsion gels prepared at a lower shear rate. For the latter, the chance is much higher that polymer/NP adsorption can keep up with the increase in interfacial area during emulsification, strongly hindering bridging [R4]. Any differences/similarities could provide more insights into the mechanism at play in the system described in the manuscript.
Finally, there is the option to simply drop the claim with regards to bridging. I believe the first claim for the facile synthesis of particulate emulsion gels, in particular in combination with the proof-of-concept, is sufficiently strong and diligently investigated to stand fully on its own.

[R1] Cui, M.; Emrick, T.; Russell, T.P. Stabilizing Liquid Drops in Nonequilibrium Shapes by the Interfacial Jamming of Nanoparticles. Science 342 (2013) 460

[R2] Lee, M. N.; Chan, H. K.; Mohraz, A. Characteristics of Pickering Emulsion Gels Formed by Droplet Bridging. Langmuir 28 (2012), 3085–3091

[R3] Bizmark, N.; Ioannidis, M.A. Nanoparticle-stabilised emulsions: droplet armouring vs. droplet bridging. Soft Matter 14 (2018) 6404

[R4] French, D.J. ; Taylor, P. ; Fowler, F.; Clegg, P.S. Making and breaking bridges in a Pickering emulsion. Journal of Colloid and Interface Science 441 (2015) 30–38

Reviewer #4

(Remarks to the Author)
"I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts."

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
All questions have been addressed clearly and the manuscript has been revised accordingly. The manuscript is recommended for publication in Nature Communication.

Reviewer #2

(Remarks to the Author)
The manuscript by Wan et al. describes a simple and effective interfacial engineering method that utilizes polymers to precisely program the interfacial assembly of nanoparticles to achieve emulsion gels bridged by a monolayer of surface-sharing nanoparticles. The method avoids the complex steps of emulsification, gelation and surface modification of NPs.The results provide new directions for synthesizing next-generation emulsion gel materials from structured soft templates. After comments were made, the additional experiments related by the authors were carefully performed and clearly expressed. The manuscript is recommended for publication in Nature Communications.

Reviewer #3

(Remarks to the Author)
After careful review of the authors' replies we find our previously stated scientific concerns sufficiently resolved. The scientific quality of the manuscript warrants publication.

However, we also note that the quality of writing in the manuscript is only satisfactory. The storyline behind the text is hard to follow, the grammar is incorrect at several instances, and parts of the text contain long lists of numbers. We found the manuscript difficult to read and have the impression that laymen will find it more difficult to comprehend. Additionally, at several instances, the text contains very definite interpretations of the data. We recommend to moderate the language by summarizing the evidence found, and stating that this evidence suggests/implies the interpretations provided by the authors.

Reviewer #4

(Remarks to the Author)
I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature

Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Responses to Reviewers' comments

Reviewer #1

Emulsion gels with a network of droplets play an important role in fields of cosmetics, foods and drugs, due to their ability on large-amount encapsulation and on-demand delivery. The manuscript by Wan et al. describes a simple, effective interfacial engineering approach, which utilizes a polymer to precisely program the interfacial assembly of nanoparticles, achieving emulsion gels bridged by facet-shared nanoparticle monolayers. The approach avoids complicated steps of emulsification, gelation and surface modifications of NPs. The system is versatile, where a wide library of chemistries is accessible in the formation of emulsion gels, facilitating their applications. Based on this, the authors prepare a sunscreen for skin protection. Encapsulated bioactive ingredients show better performances than commercial products.

The results are interesting. The interfacial 45° three-phase contact angle of polymer-tailored nanoparticles is suggested to be an important parameter in the formation of bridged emulsion gels than the well-defined surface chemistry of nanoparticles. The studies reveal important fundamental aspects of the emulsion gel formation. The results open up new avenues for the synthesis of next-generation emulsion gel materials from the structured soft templates. The experiments are done carefully, and the presentation is clear. The manuscript is recommended for publication in Nature Communications. Some minor comments are suggested below.

Reply: We are truly appreciative of the referees' very insightful and positive comments—and provide responses to the referees' criticisms below.

#1. (1) In Figure 1a, why does the addition of nanoparticles to the aqueous solution (0.5% w/w) result in a reduction in γ (~ 34.5 mN m^{-1}) as compared to that between pure water and toluene (~ 36 mN m^{-1})?

Reply: The reduction of interfacial tension between aqueous solution and toluene is due to the change of the system.

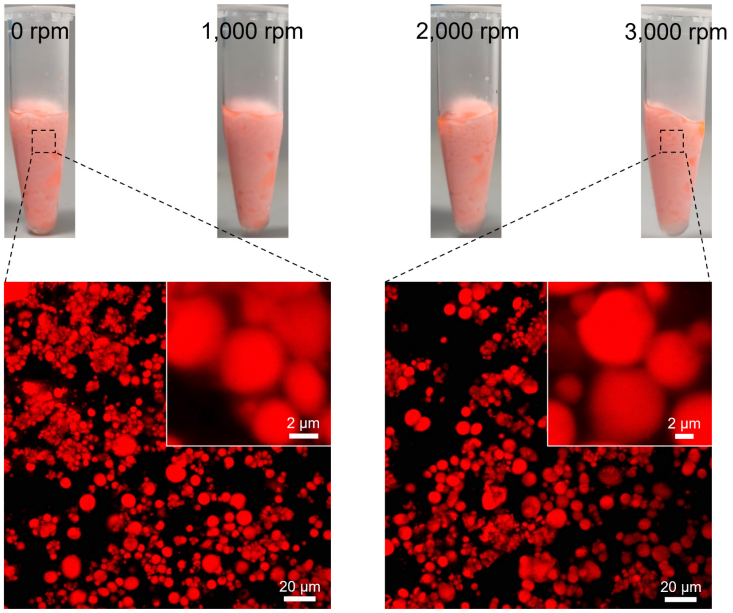
#1. (2) Some related papers on interfaces are suggested, such as Chin. Chem. Lett. 2022, 33, 3973 and Chin. Chem. Lett. 2023, 34, 107738.

Reply: We cite one of the most relevant papers from these in the revised manuscript (reference 9, *Chin. Chem. Lett.* **2023**, *34*, 107738).

#1. (3) How is the stability of the emulsion gels? Will it be stable below zero degree? Will it be stable against high-speed centrifugation?

Reply: We believe that the reviewers missed some details in our manuscript. We stated "bridged emulsion gels that show long-term stability over 12 months" and "all the emulsion gels show …, and freeze-thaw stability (–23 °C)" in line 168, page 9 and line 354, page 17, respectively. And,

according to the reviewers' question, we have supplemented the experiments that probe the bridged emulsion gels' stability against centrifugation (over 3,000 rpm), showing a strong tolerance (see the figure below). We have added this data in the revised Supplementary Information (Supplementary Fig. 21), and added relevant description in the revised manuscript.



Supplementary Fig. 21. Bridged emulsion gels are stable against centrifugation.

#1. (4) Will the addition of drugs influence the stability of the emulsion gels?

Reply: We believe that if the drug does not influence (at least not weak) the interaction between the nanoparticle and the polymer, the emulsion gels are robust just as we demonstrated in Figs. 4 and 5.

#1. (5) The format should be consistent throughout the manuscript. For example, MW = 1,000 g mol^{-1}.

Reply: We have corrected the format that the referees pointed out, as marked yellow in the manuscript. We also checked the entire text.

#1. (6) There are some typos, for example, PDSM-NH$_2$.

Reply: We have corrected "PDSM-NH$_2$" with "PDMS-NH$_2$" in line 229, page 12.

Reviewer #2

In this manuscript, the authors reported a simple strategy utilizing a polymer (PDMS-NH_2) to modulate the assembly of nanoparticles (NPs) at the water/oil interface. This approach obtained a 45° three-phase contact angle for the nanoparticles, which allowed them to cross the interface of the oil emulsion and eventually form an interconnected macroscopic network. Their bridging backbone and rheological properties could be tuned over a wide range. This method of assembly was simple and efficient and could be widely used in different biomedical scenarios. However, there are still some problems as follows before published:

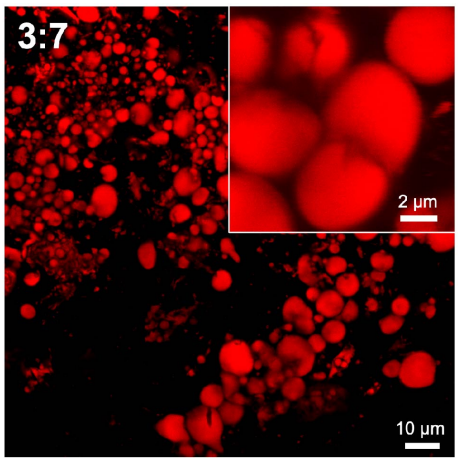
Reply: We thank the referees for the very positive comments.

#2. (1) The scale of the fluorescence images in Fig. 2 should be kept consistent, as in the localized magnification in Fig. 2a (i) as well as in Fig. 2b (ii). In addition, Fig. 2b (ii) also needs to be provided with a localized magnification for consistency.

Reply: We show these fluorescence images to clearly visualize the global interconnected skeleton of the emulsion gels (low magnification) and their zoomed-in local bridged structures (high magnification). Since the droplet size varies with the concentration of either the polymer or the nanoparticle, we employed different scales. For example, in the localized magnification in Fig. 2a (i), if the scale bar is similar to that of Fig. 2a (ii) or Fig. 2b (ii), there might be only one or partial droplet in the ken, and bridged structures are not visible. Fig. 2b (ii) shows a normal emulsion with very large droplet sizes. Besides, we analyzed the average droplet size of each fluorescence image for direct comparison in the original manuscript.

#2. (2) Supplementary Fig. 10 Whether the 3:7 scale localized magnified confocal microscopy results provide a clearer picture.

Reply: We have replaced it with a clearer one, as shown in the figure below.



Confocal microscopy images of bridged emulsion gels formed by polymer–NP ensembles with the volume ratio of the water to the oil phase of 3:7. [SiO_2 NPs] = 4% *w/w*, [PDMS-NH_2] = 3% *w/w*.

#2. (3) The encapsulation rate and loading capacity of emulsion gels as a carrier form for model bioactive molecules are two important metrics when applied. Please add relevant experiments.

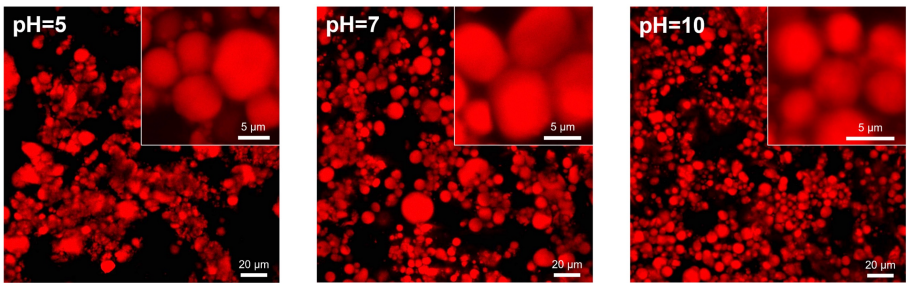
Reply: We agree with the referees' comments and have added the encapsulation rate and loading capacity of the bridged emulsion gels as the carrier for β-carotene (the model bioactive molecules selected in our work) in the revised Supplementary Information. As presented in Supplementary Table 1, the emulsion gels (samples used in Fig. 4) show high encapsulation rates (over 97%), demonstrating a few free oil phases left (verified by the inverted sample in Fig. 2c), and have a decreasing trend of loading capacity with C_N (the concentration of the nanoparticles).

Supplementary Table 1. The encapsulation rate and loading capacity of bridged emulsion gels as the carrier for β-carotene with different C_N. [C_P] = 3% *w/w*, water/oil ratio is 3:7 (*v/v*).

Different C_N	Encapsulation rate (%)	Loading capacity (μg/mg)
1 % *w/w*	97.03 ± 0.61	170.48 ± 1.07
2 % *w/w*	97.97 ± 0.47	86.07 ± 0.41
4 % *w/w*	98.69 ± 0.37	43.34 ± 0.16

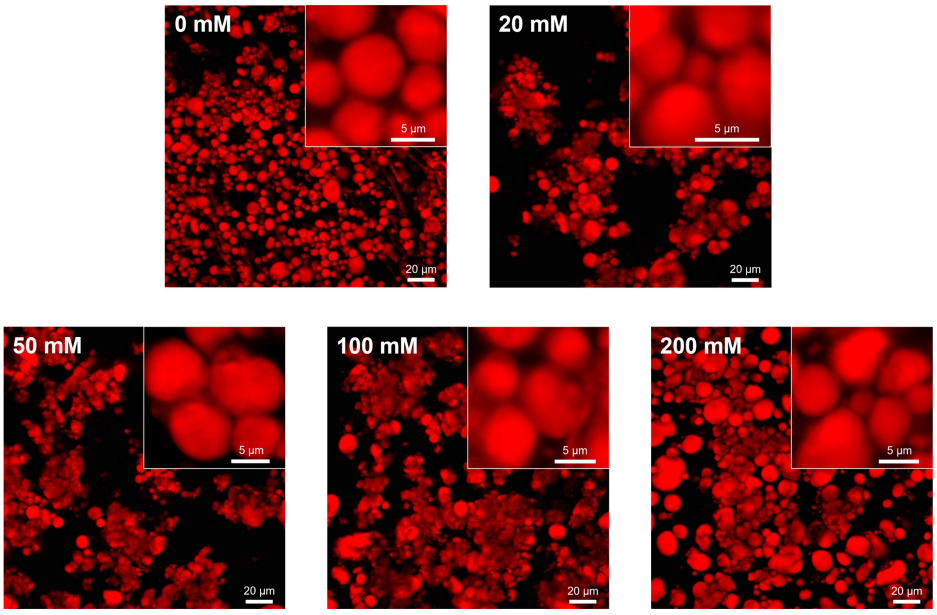
#2. (4) Due to the extremely wide range of biomedical applications and higher requirements for emulsion gel stability in different environments, please supplement the pH stability and ion concentration stability experiments of emulsion gels.

Reply: We have added the pH stability and ion concentration stability of bridged emulsion gels in the revised Supplementary Information (Supplementary Figs. 19 and 20). As shown in Supplementary Fig. 19, bridged emulsion gels are stable over a wide range of pH (5–10), and are destroyed at pH 3 (unstable emulsions). The disruption at lower pH value derives from weakened and even none electrostatic interaction between SiO_2 NPs and PDMS-NH_2, where p*K*a of the surface negative charge group of SiO_2 NPs is 4–5 and the decrease of the surface charge quantity is verified by the zeta potential results (Supplementary Fig. 2).



Supplementary Fig. 19. Bridged emulsion gel systems formed by polymer–NP ensembles at different pH. [SiO_2 NPs] = 4% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 5:5 (*v/v*).

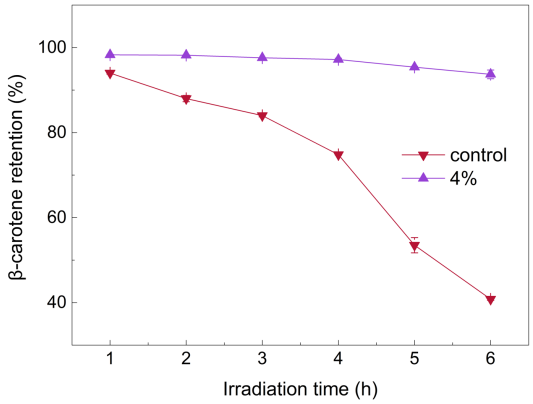
Moreover, bridged emulsion gels showed high stability against ionic strength and the droplet size did not vary appreciably even at NaCl concentrations of 200 mM, confirming their promising application for biomedical applications. (Supplementary Fig. 20).



Supplementary Fig. 20. Bridged emulsion gel systems formed by polymer–NP ensembles with different ionic strengths (NaCl). [SiO_2 NPs] = 4% *w*/*w*, [PDMS-NH_2] = 3% *w*/*w*, water/oil ratio is 5:5 (*v*/*v*).

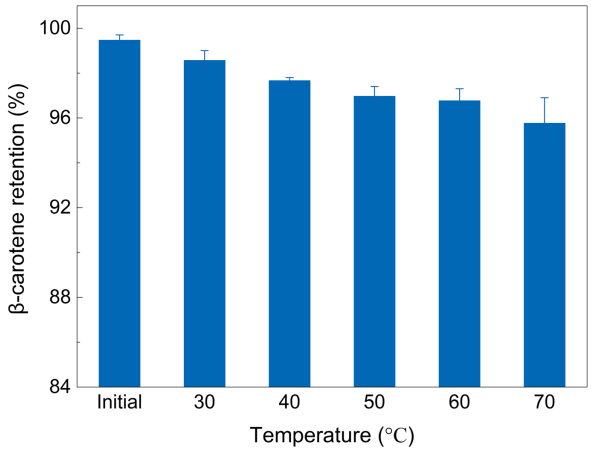
#2. (5) In this study, β-carotene was chosen as a model bioactive molecule. However, there is not enough research content on the stability of β-carotene related to its use to protect the skin from UV irradiation damage. Please add experiments related to UV stability and thermal stability of emulsion gels encapsulating β-carotene.

Reply: As shown in Supplementary Fig. 24, for the control sample, the retention of β-carotene decreased significantly over irradiation time and was less than 41.0% after 6 h, suggesting a continuous, strong UV degradation of β-carotene. In stark contrast, β-carotene encapsulated in bridged emulsion gels exhibited enhanced UV stability with a retention of 93.7% following a 6 h duration of UV exposure. In the emulsion gel system, the jamming interfacial layer of polymer–NP ensembles enclosed the β-carotene within oil droplets and impeded direct UV irradiation, thereby significantly diminishing the likelihood of β-carotene degradation.



Supplementary Fig. 24. The retention of β-carotene loaded in the dispersed oil phase of bridged emulsion gels under ultraviolet irradiation. [SiO_2 NPs] = 4% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 3:7 (*v/v*). Bulk oil loaded with the same content of β-carotene served as the control. Data are presented as mean values ± SD.

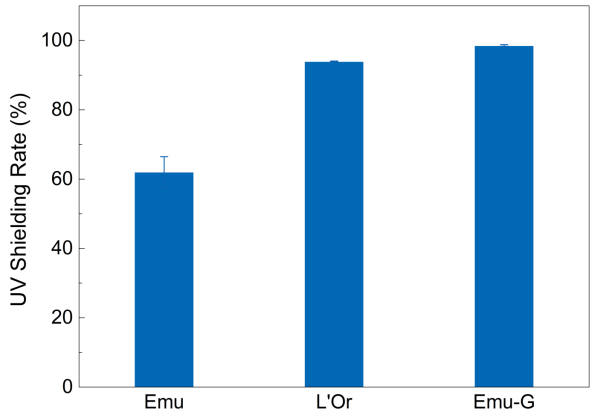
Additionally, we examined the retention of β-carotene encapsulated in bridged emulsion gels after treatment at different temperatures as it is unstable at high temperatures (*Food Chemistry* **2012**, *132*, 1221–1229) (Supplementary Fig. 25). The jamming interfacial layer provided notable thermal protection on β-carotene, the retention of which still maintained 95.8% heated at 70 °C. Experiment details and discussions have been provided in the revised manuscript and Supplementary Information.



Supplementary Fig. 25. The retention of β-carotene loaded in the dispersed oil phase of bridged emulsion gels after treatment at different temperatures. [SiO_2 NPs] = 4% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 3:7 (*v/v*). Data are presented as mean values ± SD.

#2. (6) UV shielding rate measurement is also an important test for emulsion gel systems used for skin UV protection.

Reply: We have added the UV shielding rate measurement of emulsion gels in the revised Supplementary Information (Supplementary Fig. 28). The results indicate that the emulsion gel could effectively absorb/scatter > 98.5% UV light, while the UV-shielding rate of L'Oreal sunscreen sample and emulsion sample were respective 94.0% and 62.1%, suggesting the effective UV-shielding performances of emulsion gel systems.

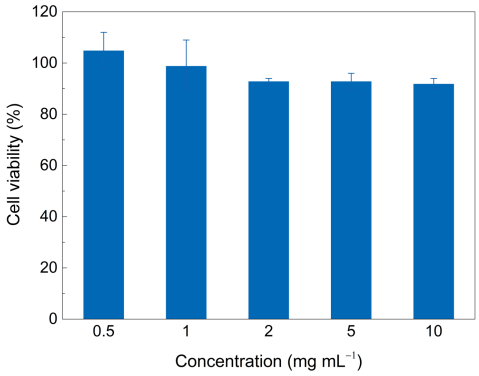


Supplementary Fig. 28. UV shielding rate of emulsion, L'Oreal sunscreen, and emulsion gel samples. Data are presented as mean values ± SD.

#2. (7) Prior to animal experiments, please add relevant in vitro cytological evaluations:
1) Cytotoxicity testing of emulsion gels.
2) Emulsion gel for keratin-forming cell protection and inhibition of UV-induced ROS production.
3) Effect of emulsion gels on mitochondrial membrane depolarization.

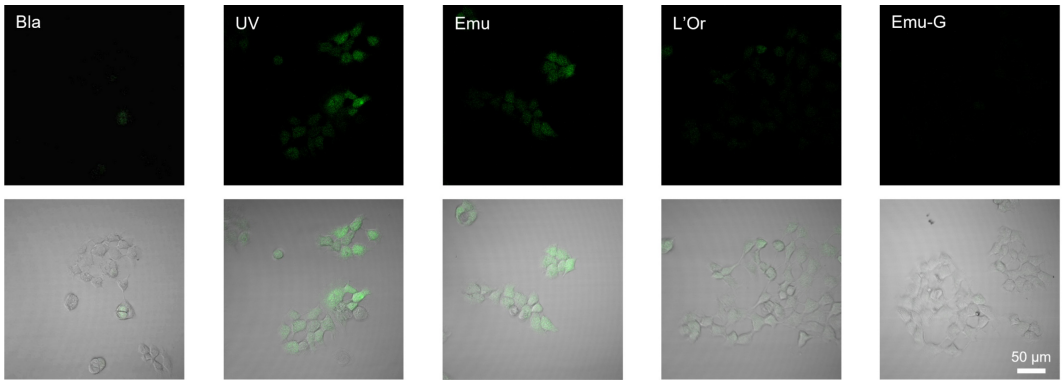
Reply: We have added these in vitro cytological evaluations in the revised manuscript and Supplementary Information.

1) The cytotoxicity of emulsion gels on the human keratinocyte cell line (HaCaT) was assessed using Cell Counting Kit-8 (CCK-8) assay. As shown in Supplementary Fig. 26, the cell viability after treatment with emulsion gels was greater than 92%, indicating that emulsion gels were nontoxic.



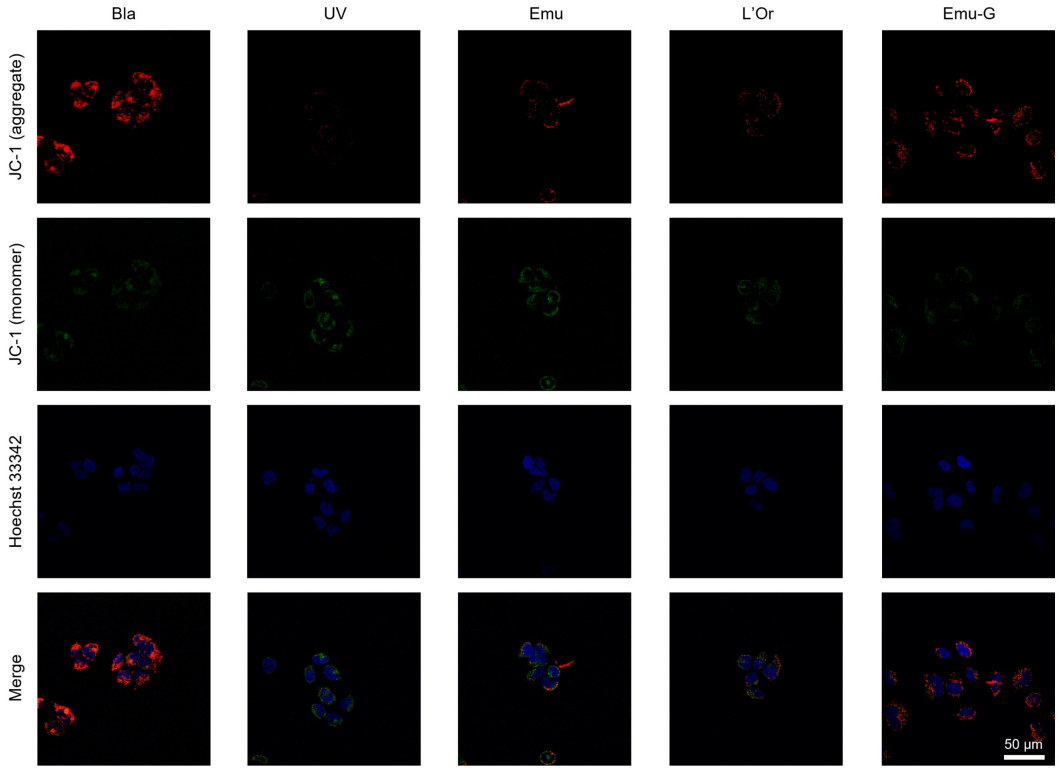
Supplementary Fig. 26. In vitro cytotoxicity of emulsion gels at different concentrations on HaCaT cells expressed as cell viability (%). Data are presented as mean values ± SD.

2) To evaluate the inhibition behaviors against UV-induced ROS production of emulsion gels, 50 mg sample was applied to a thin quartz sheet fixed at 1 cm above the HaCaT cell culture dishes, exposed to 270 mJ cm^{-2} Ultraviolet A (UVA) (365 nm), and the production of ROS was tracked using an oxidation-sensitive fluorescent probe. As shown in Supplementary Fig. 27, UV irradiation dramatically enhanced ROS production in unprotected HaCaT cells. For the emulsion group, the cells also produced a high level of ROS. With the cover of L'Oreal sunscreen, the level of ROS was remarkedly diminished. Most importantly, there was almost no ROS generation in the emulsion gel group (as same as the blank group), which is likely attributed to its excellent UV-shielding performances.



Supplementary Fig. 27. Fluorescent confocal microscope images of HaCaT cells covered with different protective samples followed by UV irradiation and incubating with oxidation-sensitive fluorescent probe (carboxy-H2DCFDA), showing ROS generation and in vitro UV protection effect. Bla represents the blank group, that cells were neither covered with samples nor irradiated with UV spot. UV represents the UV group, that cells were treated with UV irradiation. Emu, L'Or, and Emu-G represent the emulsion, L'Oreal and emulsion gel groups, that cells were covered with the same amount of emulsion, L'Oreal sunscreen, and emulsion gel sample before UV irradiation, respectively.

3) It is known that UV-induced ROS could cause oxidative stress and mitochondrial membrane depolarization, leading to apoptosis. (*Adv. Funct. Mater.* **2018**, *28*, 1802127). Next, we examined the mitochondrial damage in the above five groups of HaCaT cells, to further confirm the ROS inhibition efficiency of the emulsion gels. The integrity of the mitochondrial membrane potential (ΔΨm) could be detected *via* JC-1 staining. As shown in Supplementary Fig. 29, HaCaT cells showed decreased red fluorescence and increased green fluorescence after UV irradiation, indicating the decrease in ΔΨm and mitochondrial membrane depolarization. With the cover of emulsion gels, there was almost no mitochondrial membrane depolarization, showing the best protection effects compared to the L'Oreal product and emulsion.



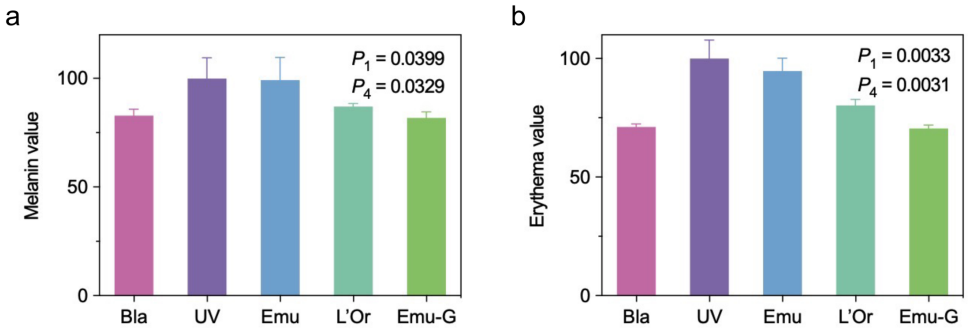
Supplementary Fig. 29. Effects of different samples protection on mitochondrial membrane depolarization induced by UV irradiation of HaCaT cells. Bla represents the blank group, that cells were neither covered with samples nor irradiated with UV spot. UV represents the UV group, that cells were treated with UV irradiation. Emu, L'Or, and Emu-G represent the emulsion, L'Oreal and emulsion gel groups, that cells were covered with the same amount of emulsion, L'Oreal sunscreen, and emulsion gel sample before UV irradiation, respectively. Red fluorescence indicates the mitochondrial aggregated form of JC-1 due to a high mitochondrial membrane potential (ΔΨm), whereas green fluorescence represents the monomeric form of JC-1 due to low ΔΨm, and blue fluorescence suggests the nuclei.

#2. (8) The following experiments and indicators still need to be added to the animal model of protecting the skin from UV radiation damage:
1) Relative melanin and relative erythema values for each group of mice at the end of UV treatment.

2) Relative epidermal thickness and relative keratin percentage in each group of mice at the end of UV treatment.

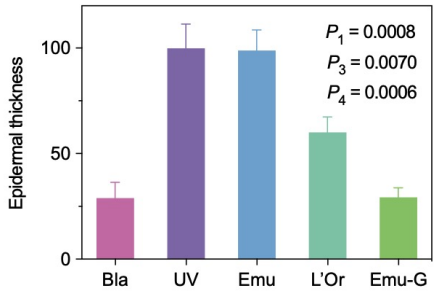
Reply: We have added these experiments and relevant discussions in the revised manuscript and Supplementary Information.

1) Supplementary Fig. 30 showed relative melanin and erythema values for each group of mouse skin after UV treatment. It was found that the mouse skin was severely damaged after UV irradiation without any protection, exhibiting much higher levels of melanin and erythema (from 83 to 100, and from 71 to 100, respectively). For the emulsion group, there was still a large amount of melanin and erythema (99 and 95, respectively), showing negligible protection on the skin due to the encapsulated active substances' quickly flowing away. The melanin and erythema values were reduced when the L'Oreal sunscreen was applied (87 and 80, respectively), showing a certain protection on the skin. More importantly, the melanin and erythema values of the skins of protected mice by emulsion gels (82 and 71, respectively) were almost identical to the values of the blank group, indicating their effective resistance to strong UV exposure.



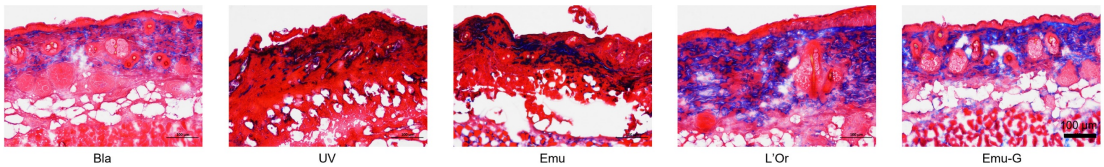
Supplementary Fig. 30. a Relative melanin value of mouse skin swabbed with different protective samples followed by UV irradiation. **b** Relative erythema value of mouse skin swabbed with different protective samples followed by UV irradiation. Data were collected based on the normalization of the UV group (directly UV irradiation sample) as 100 and presented as mean ± s.e.m. of n = 3 biologically independent mice. P value showing the statistically significant difference between the two sets of values, consistent with Fig. 5 in the manuscript. Bla represents the blank group, that mice were neither coated with samples nor irradiated with UV spot. UV represents the UV group, that mice were treated with UV irradiation. Emu, L'Or, and Emu-G represent the emulsion, L'Oreal and emulsion gel groups, that mice were swabbed with the same amount of emulsion, L'Oreal sunscreen, and emulsion gel sample before UV irradiation, respectively.

2) The epidermal thickness for each group of mouse skin after UV treatment was also monitored. As shown in Supplementary Fig. 31, the mouse skin of the UV group and the emulsion group exhibited a pronounced epidermal hypertrophy effect compared to the blank group (from 29 to 100 and 99, respectively), which could be markedly diminished by L'Oreal sunscreen (epidermal thickness of 60), whereas the thickness of emulsion gels-protected skins (29) kept the original level with the blank.

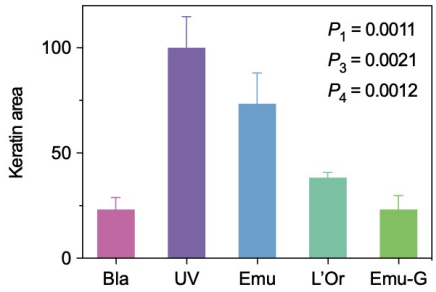


Supplementary Fig. 31. Relative epidermal thickness of mouse skin swabbed with different protective samples followed by UV irradiation. The epidermal thickness of the injured area was measured using ImageJ based on H&E staining images. Data were collected based on the normalization of the UV group (directly UV irradiation sample) as 100 and presented as mean ± s.e.m. of n = 3 biologically independent mice.

3) The effective anti-UV protection of the emulsion gels was consistent with the observations of the keratinized areas of the mouse skin after trichrome staining (Supplementary Figs. 32 and 33). Compared with the blank group (23), the skin tissues of mice demonstrated varied levels of keratin overproduction in the UV group, emulsion group, and L'Oreal group (100, 73, and 38, respectively), while no discernible phenomena were observed in the skins coated with emulsion gels (23).



Supplementary Fig. 32. Trichrome staining of skin sections from the irradiated areas of five groups of mice collected on 3rd day.



Supplementary Fig. 33. Relative keratin percentage of mouse skin swabbed with different protective samples followed by UV irradiation. The keratin percentage of the injured area was measured using ImageJ based on trichrome staining images. Data were collected based on the normalization of the UV group (directly UV irradiation sample) as 100 and presented as mean ± s.e.m. of n = 3 biologically independent mice.

Reviewer #3

The manuscript NCOMMS-24-27831 by Wan et al. introduces a facile method for the synthesis of particulate emulsion gels through polymer-mediated interfacial assembly of nanoparticles. While this mechanism of emulsion stabilization is not novel (R1, Science 2013, 342, 460–463), its implementation for the synthesis of particulate emulsion gels can be considered so. The authors extensively characterised the synthesized particulate emulsion gels with a variety of complimentary experimental techniques suitable for the material (e.g. confocal microscopy, oscillatory rheology). Through an interdisciplinary approach, the authors additionally provide an interesting proof-of-concept through the encapsulation and subsequent release of sunscreen ingredients in the synthesized particulate emulsion gels. However, I believe the claim of achieving specifically a bridged emulsion gel over the entire presented experimental range is not sufficiently substantiated. If this issue is addressed (vide infra), I would consider this manuscript suitable for publication in Nature Communications.

Following is a more detailed discussion on the points described above, in addition to recommendations on how to potentially address the mentioned issues.

Reply: We appreciate the referees' positive comments – and address each of the referees' comments below.

#3. (1) The manuscript contains two distinct claims. The first is the facile synthesis of a particulate emulsion gel, brought about by polymer-regulated interfacial assembly of nanoparticles. The second is that, over a wide range of experimental conditions, the emulsion droplets are connected through nanoparticle bridges consisting of only a single monolayer. I believe it warranted to address both of these claims separately.

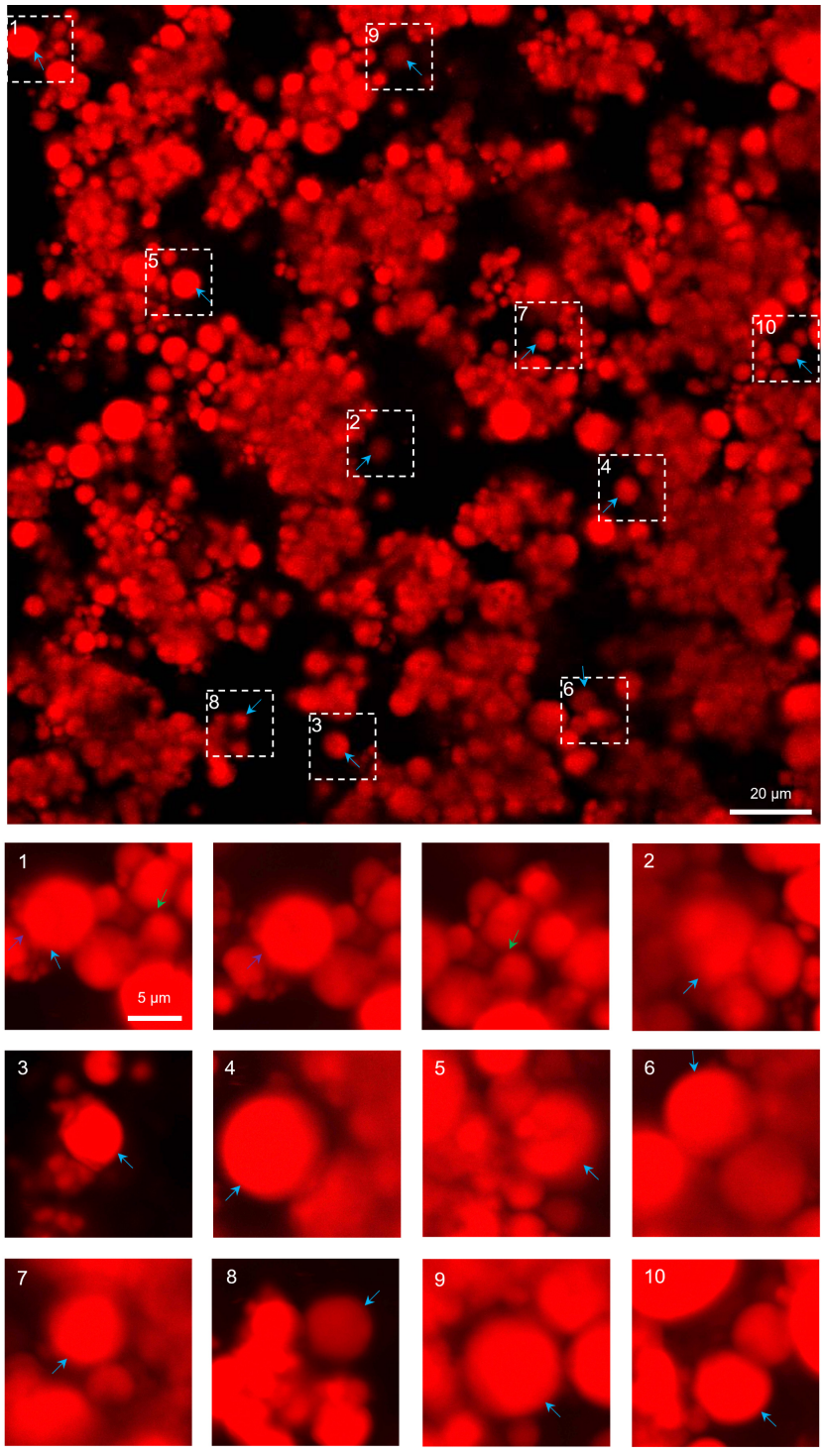
The work presented in the manuscript fully supports the first claim. The combination of confocal microscopy and oscillatory rheology makes it abundantly clear that emulsion particulate gels have been formed over a wide range of experimental conditions, simply through shearing the loaded oil and water phases. While the proposed mechanism of emulsion droplet stabilization through nanoparticle/polymer assemblies is not novel (R1, Science 2013, 342, 460–463), its application for the synthesis of particulate emulsion gels could be considered so. Additionally, the manuscripts provides a very interesting proof-of-concept through the encapsulation and subsequent release of some of the active compounds of sunscreen. As it is outside by expertise I will refrain from making comments on the histological analysis shown in the manuscript, but the concept looks promising.

Reply: We appreciate the referees' positive comments and addressed the raised questions point-by-point below.

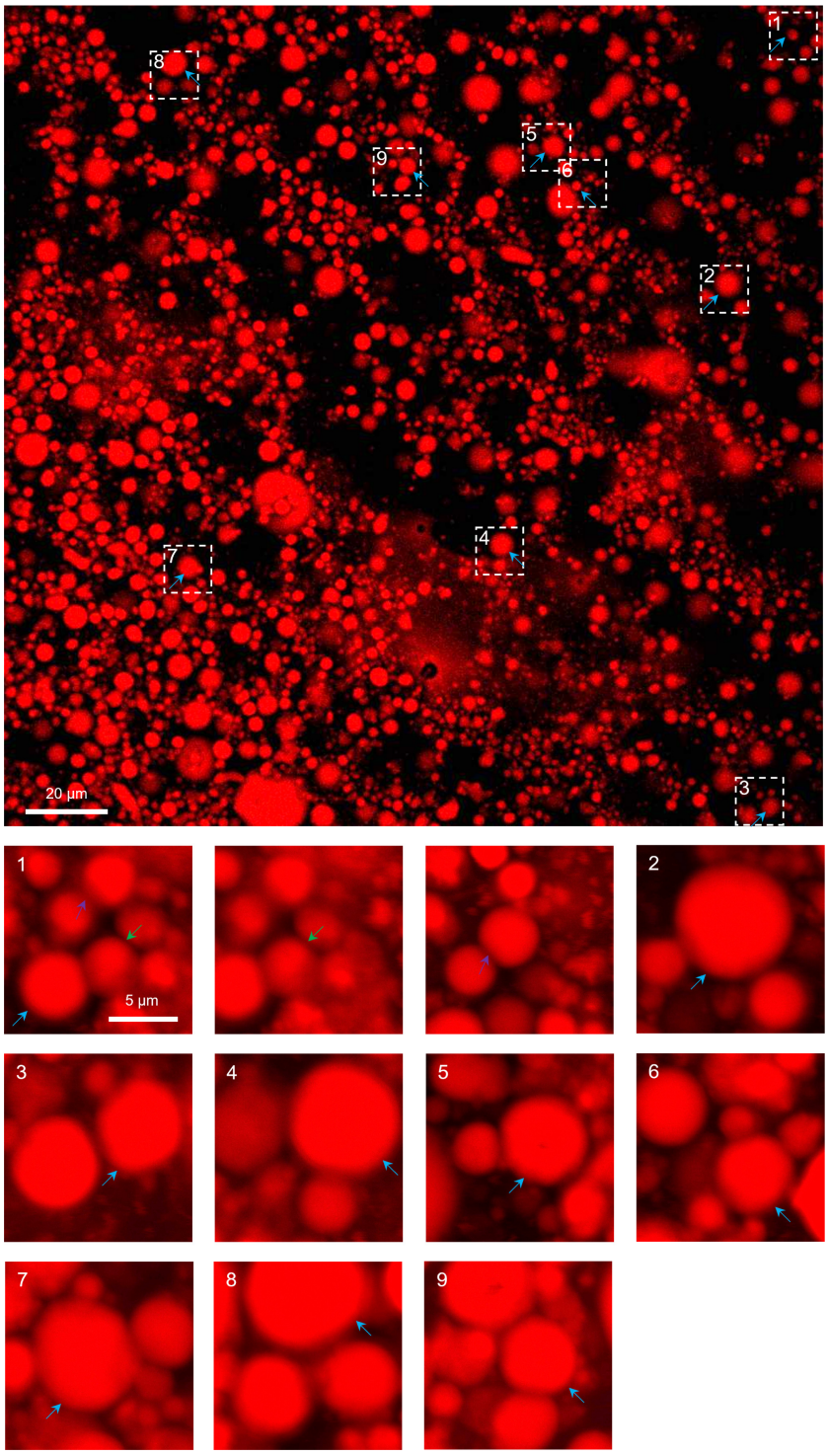
#3. (2) My main concerns, however, lie with the second claim. In my opinion, the work presented in the manuscript does not sufficiently substantiate the claim that the emulsion droplets are bridged through nanoparticle monolayers over the entire range of experimental conditions.

In particular, there appear to be consistent differences between experimental findings for the emulsion particulate gels with less than 2wt% nanoparticles in the aqueous phase compared to those with higher nanoparticle content. For example, whereas the confocal image in Figure 2a shows that the oil droplets in the polymer/NP ensemble with 2 wt% nanoparticles display the distinct, polygonal shape associated with bridging (R2, Langmuir 2012, 28, 3085–3091), this is notably much less the case for the other confocal images (with higher NP content) in Figure 2 and Figure 1c.

Reply: It is clear that bigger NP monolayer bridged emulsion gels have a clear emulsion droplet outline due to the visible NPs (Fig. 1d). For the smaller NP case, the emulsion droplet outline is much dimmer due to the fluorescence oil phase, especially for the smaller droplet cases that are stabilized by higher NP loading. These are the cases that the referees mentioned in Figs. 1c, 2a(ii), 2b(i), and 2d(i). Thus, we here dissect a confocal image of emulsion gels that are prepared by 4% *w/w* NPs and 3% *w/w* PDMS-NH_2 (the same assembly parameters but different batches), with 12 zoomed-in images, as shown in Supplementary Fig. 9. Specifically, we focus on zones that seem to be isolated droplets in low magnification image and at the edges of emulsion gels (where this image is a typical area that looks like a lot of isolated droplets). One can see that all of these zoomed-in images show polygonal shape of the droplets and their close-compacted features. Different zoomed-in images may refocus to see clearer the boundary between droplets, as shown in zoomed-in 1. Additionally, the emulsion gels prepared from much higher NP loading (8% *w/w*) have similar features (Supplementary Fig. 10). Therefore, the emulsion gels fabricated over our entire range of experimental conditions (phase diagram in Fig. 2) do have NP monolayer shared structures.



Supplementary Fig. 9. A confocal image and the corresponding 12 zoomed-in images of emulsion gels formed by polymer–NP ensembles. [SiO_2 NPs] = 4% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 5:5 (*v/v*). To clearly visualize the three-dimensional structure of the emulsion gels, some zoomed-in images have been refocused (To view the interface, certain droplets are not clear). The blue arrow shows the same droplet before and after zoomed-in, and the purple and green arrows mark the same boundaries.



Supplementary Fig. 10. A confocal image and the corresponding 11 zoomed-in images of emulsion gels formed by polymer–NP ensembles. [SiO_2 NPs] = 8% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 5:5 (*v/v*). The blue arrow shows the same droplet before and after zoomed-in, and the purple and green arrows mark the same boundaries.

On that account, we use clearer images to replace the originals in Fig. 2a(ii), Fig. 2b(i) and Fig. 2d(i).

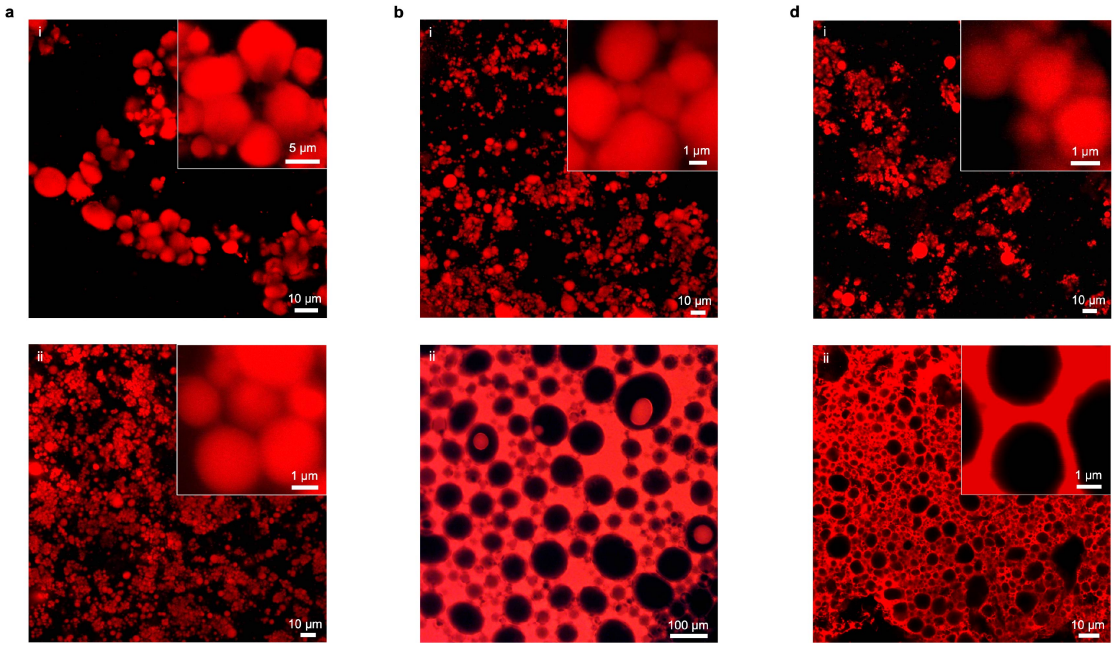


Fig. 2 | Impact of altering the particle and polymer concentration, and the water/oil volume ratio upon system morphology. a Bridged emulsion gel systems formed by polymer–NP ensembles with a NP concentration of (i) 2% *w/w* and (ii) 8% *w/w* at a fixed concentration of PDMS-NH_2 (3% *w/w*). Water/oil ratio is 5:5 (*v/v*). **b** Emulsion systems formed by polymer–NP ensembles at constant NP concentration (4% *w/w*) with varying concentrations of PDMS-NH_2 from (i) 1% *w/w* to (ii) 10% *w/w*. Water/oil ratio is 5:5 (*v/v*). **d** Emulsion gel systems formed by polymer–NP ensembles with the volume ratio of the water to the oil phase of (i) 8:2 and (ii) 2:8. [SiO_2 NPs] = 4% *w/w*, [PDMS-NH_2] = 3% *w/w*.

#3. (3) Additionally, Figure 3e gives the impression of two distinct scaling regimes for the zero-shear storage modulus and yield stress in the low and high regions of nanoparticle weight fraction, where the latter one has a higher power-law exponent compared to the former (indicating different droplet-droplet interaction). While I agree with the authors that the described power-law behaviour of the highlights the uniqueness of the system compared to others (R2, Langmuir 2012, 28, 3085–3091), I do not believe it unambiguously supports the notion of continuous droplet bridging over the presented experimental range.

Reply: Mohraz *et al.* made a deeper contribution to the rheology of bigger NP alone bridged emulsion gels with respect to particle volume fraction (*Soft Matter* **2017**, *13*, 2513–2522) on the basis of R2 the referees mentioned (*Langmuir* **2012**, *28*, 3085–3091). Comparing the data between our results and theirs finds that our scaling regime for the zero-shear storage modulus over NP loading is located in the lower NP region or region I in Fig. 4 of the *Soft Matter* Reference (for convenient comparison, we changed axes to linear as shown in the figure below). According to their theory, in the lower NP region in compartmentalization of zero-shear storage modulus vs NP loading, there are no isolated emulsion droplets.

The other that we need to note is our system is totally different from the works done by Mohraz *et al*. In our system, the adsorption of NPs recruited by the polymers, as we stated in line 159, page 8 in our manuscript, is much faster than the NPs alone used in their works. The mechanism is totally different (details see below), such that our system has uniqueness of scaling law of the zero-shear storage modulus and yield stress *vs* nanoparticle weight fraction, due to the assembly mechanism in forming NP monolayer bridged structures and the strong entanglement of polymers.

Additionally, the appearance of our samples shows > 97% gels (like the inverted vial in Fig. 2c), further demonstrating the continuous droplet bridging in our phase diagram (Fig. 2c).

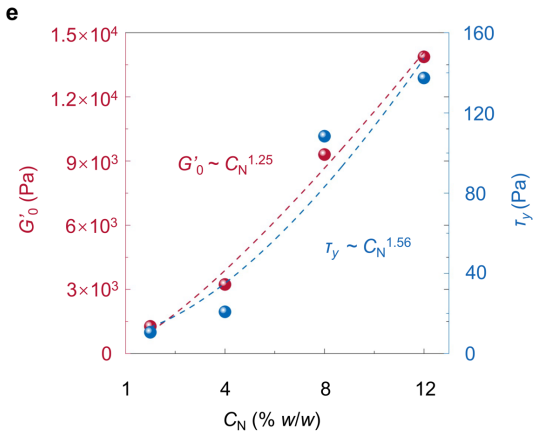
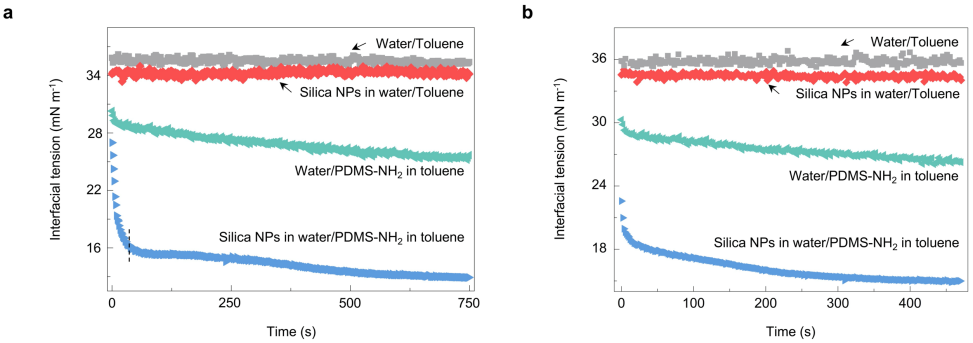


Fig. 3e. Scaling of G'_0 and yield stress, τ_y, of bridged emulsion gels with C_N. $[C_P]$ = 3% *w/w*, water/oil ratio is 5:5 (*v/v*).

#3. (4) Another issue for the claim of bridged emulsion droplets is that the extrapolate findings from systems with much larger, nicely spherical nanoparticles (diameter 630 nm) to systems made with the much smaller, commercial Ludox HS-40 nanoparticles (diameter 12 nm). While droplet bridging has been extensively studied for particles in the former size-range, this is not the case for the latter. In particular, for the smaller Ludox particles the exact value of the contact angle (along with pH and ionic strength) is expected to play a much more crucial role in their ability to form bridges between emulsion droplets (R3, Soft Matter, 2018,14, 6404–6408). In that regard, I find it unlikely that the found 45 degree contact angle for the large nanoparticles can be directly transposed on the smaller Ludox nanoparticles, in addition to this value being maintained over the relatively broad range of polymer concentrations described in the manuscript.

Reply: We thank the reviewers for this feedback. Bigger NPs (diameter hundred nanometers) do have been extensively used to form emulsion gels with NP monolayers shared between droplets, such as the works done by Mohraz *et al*. However, the mechanism is totally different between our system and the emulsion gels stabilized by the alone NPs' monolayers. Firstly, our NPs regardless of the size, own high negative surface charge (see our zeta potential data) and have no interfacial activity (see our interfacial tension reduction data, Figures below), while the NPs (with relatively low surface charge, *Langmuir* **2012**, *28*, 3085–3091) that were used alone to fabricate

emulsion gels in references (e.g., in works done by Mohraz *et al*.) will be adsorbed to oil/water interface. The assembly of NPs (our case) attracted by polymers is much faster than the adsorption of NPs alone system (*Science* **2013**, *342*, 460–463; *Langmuir* **2010**, *26*, 12518–12522). The kinetics of NPs approaching to oil/water interface influences, naturally, the trapped state in the evolution of emulsion droplets (Ostwald Ripening). We believe that this is the reason that our scaling regime for the zero-shear storage modulus over NP loading is located in the lower NP region in Fig. 4 of *Soft Matter* (**2017**, *13*, 2513–2522).

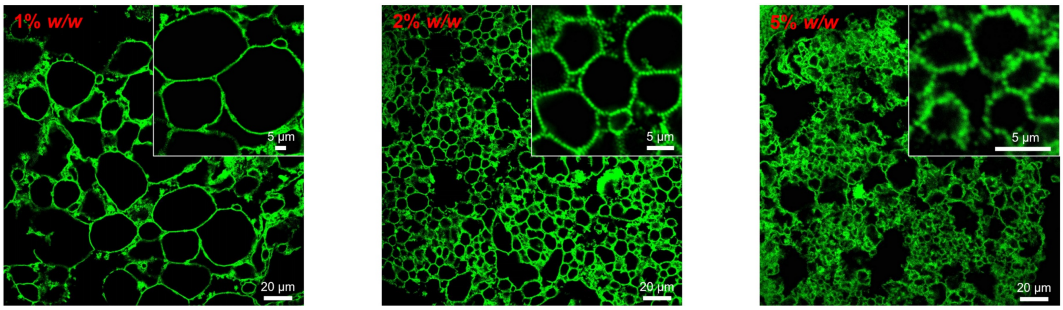


The recruitment of negatively charged **a** 12 nm SiO_2 NPs and **b** 630 nm SiO_2 NPs to the interfaces by PDMS-NH_2 occurs on different time scales and depends on the relative concentration of each. These processes can be observed by monitoring the interfacial tension as a function of time for a pendant water drop suspended in a bath of toluene for systems configured with either nothing (gray squares), SiO_2 NPs (red rhombuses), PDMS-NH_2 (green triangles), or SiO_2 NPs + PDMS-NH_2 (blue triangles).

Secondly, polymer–NP cooperative assembly in our strategy has dynamic character (*Sci. Adv.* **2020**, *6,* eabb8675*; J. Am. Chem. Soc.* **2023***, 145*, 25431–25439). The number of polymer chains anchored to the NP at the interfaces is self-regulated. In the formation of our emulsion gels, a few polymer chains assemble at the interfaces firstly, and then recruit NPs, where these polymer–NP co-assemblies have a strong tendency to cross over oil droplets (sonicated) due to their low three-phase contact angle with respect to the water phase, as we stated in the manuscript (the first and second paragraph of the Results and Discussion Section). Along with the oil emulsion droplets' evolution, NP monolayer, most part in water phase and edge with double side anchoring few polymers immersed in oil, forms and constructs the bridged networks. Because of the dynamic feature of polymer–NP co-assemblies, the effective number of polymer chains used to form monolayer bridged structures should be certain at a fixed NP concentration in a suitable range of pH (5–10), ionic strength (NaCl, 0–200 mM), or polymer concentration (see our phase diagram in Fig. 2c). This is also the novelty and uniqueness (we believe) that we do not need sophisticated syntheses of NPs to formulate 45° contact angle and then monolayer bridged emulsion gels.

Finally, we believe that transposing large nanoparticles on the smaller Ludox nanoparticles makes sense. Given the similar surface features and dynamic coassembly behavior with polymers, large NPs (8% *w/w*) can form monolayer bridged emulsion gels with ranging polymer concentrations from 1% to 5% (Fig. 1d and Supplementary Fig. 12). The polymer chain number (in our experimental range) only impacts the initial speed of polymers approaching the interfaces, but does not vary the final microstructures (or morphologies), i.e., their 45° contact angle, such that

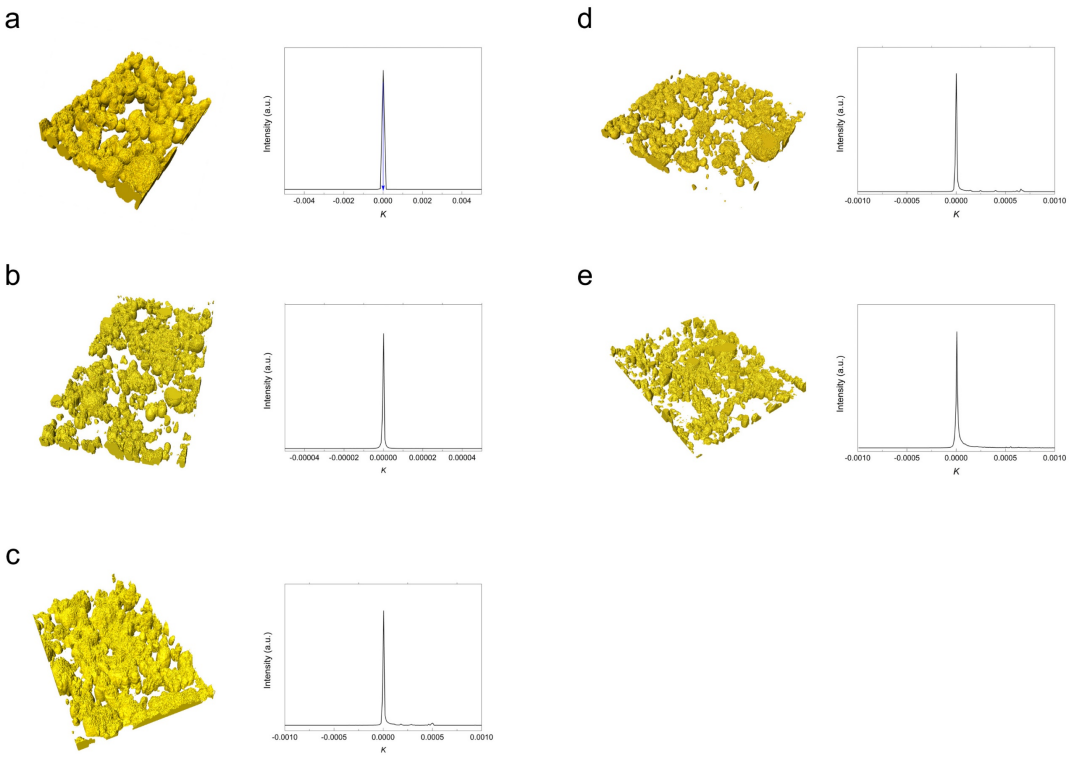
higher polymer concentration condition leads to smaller emulsion droplets based gels. Naturally, large NPs have different ranges of polymer concentration with smaller Ludox NPs, due to the different effective number chains to form 45° contact angle.



Supplementary Fig. 12. Low-magnification and high-magnification confocal microscopy images of bridged emulsion gels prepared over a broad range of PDMS-NH_2 concentrations (1%–5% *w/w*) showing a monolayer of particles bridging numbers of faceted droplets in the gel interior as the particles are tagged with RITC. [SiO_2 NPs] = 8% *w/w*, water/oil ratio is 5:5 (*v/v*).

#3. (5) Finally, I would like to provide some options to the authors for addressing my concerns with regards to the second claim. The first is to just unambiguously show the monolayer bridging of emulsion droplets for polymer/NP ensembles with higher than 2 wt% nanoparticles. A potential way to directly show this is through analysis of the Gaussian curvature of the particle surfaces in the emulsion gels [R2, Langmuir 2012, 28, 3085–3091]. An alternative (and perhaps easier) method is to compare the presented results with those from particulate emulsion gels prepared at a lower shear rate. For the latter, the chance is much higher that polymer/NP adsorption can keep up with the increase in interfacial area during emulsification, strongly hindering bridging (R4, J. Colloid Interface Sci., 2015, 441, 30–38). Any differences/similarities could provide more insights into the mechanism at play in the system described in the manuscript.

Reply: We thank the referees' suggestions. Firstly, we perform 3D imaging, surface reconstruction, segmentation, and Gaussian curvature (K) measurement to investigate the K distribution of those emulsion gels in Fig. 2 and Fig. 1c, as shown in Supplementary Fig. 14. One can see that all samples' curves show a sharp peak at $K = 0$ and their asymmetry at the right side, demonstrating that most of the droplets are planar and the droplet networks' boundaries generate the asymmetry (positive Gaussian curvature).

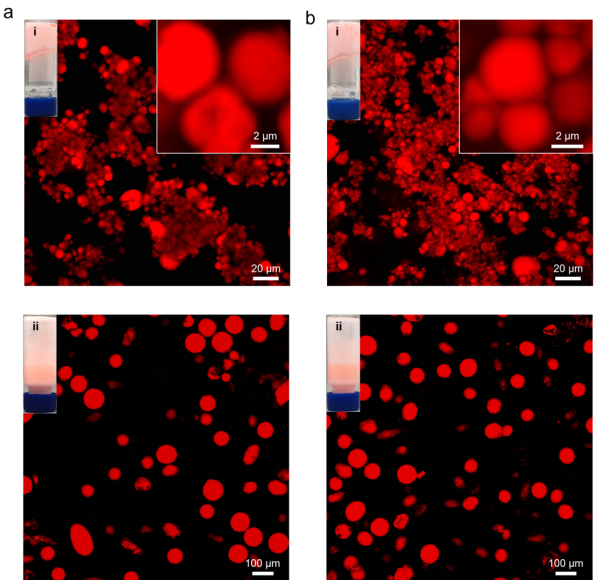


Supplementary Fig. 14. The Gaussian curvature distributions and the corresponding surface reconstructions of emulsion gel samples in Fig. 2 and Fig. 1c. **a** [SiO_2 NPs] = 2% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 5:5 (*v/v*). **b** [SiO_2 NPs] = 4% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 5:5 (*v/v*). **c** [SiO_2 NPs] = 8% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 5:5 (*v/v*). **d** [SiO_2 NPs] = 4% *w/w*, [PDMS-NH_2] = 1% *w/w*, water/oil ratio is 5:5 (*v/v*). **e** [SiO_2 NPs] = 4% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 8:2 (*v/v*).

Secondly, we prepare another batch of emulsion samples from 4% and 8% *w/w* nanoparticles using both ultrasonic and vortexed mixing methods which impose different shear rates. As shown in Supplementary Fig. 15, ultrasonication treatment yields highly stable and bridged emulsion gels composed of faceted droplet clusters regardless of NP's concentration, whereas vortex mixing produces common emulsions composed of spherical, isolated, and sparse droplets. And, the droplet size of the bridged emulsion gels is much smaller than that of the common emulsions. The reason that the two shear forces generate totally different morphologies of the emulsion can be found in the evolution and formation process of emulsions. Firstly, the emulsions evolved procedures that include: emulsion droplet generation upon oil/water mixing, polymer/NP assembly, droplet collision and coalescence until the system is trapped by the jamming of the interfacial NPs. Secondly, ultrasonication has much stronger shear force than vortex, such that the former will lead to much more, smaller droplets. As described in the Results and Discussion Section in our manuscript, a relatively low amount of polymers recruits the NPs to assemble at the interfaces, where the NPs have a low three-phase contact angle with respect to the aqueous phase, along with the evolution of the small, emulsified droplets (capillary bridge formation and coalescence), leading to the jamming of bridged emulsions, i.e., forming the bridged emulsion gels. In contrast, vortex mixing generates much fewer, larger droplets, such that less droplet

collision (as shown in Supplementary Fig. 15) happens and it will allow the isolate droplets to have enough time to be covered by the polymer–NP assemblies, thus preventing further Ostwald Ripening.

Therefore, through these two kinds of additional experiments, we believe that our emulsion gels do be a whole range of NP monolayer structured network gels.



Supplementary Fig. 15. a Confocal microscopy images of samples that prepared *via* (i) ultrasonication (46 W for 14 s continuously) and (ii) vortex mixing (3,000 rpm for 5 min). [SiO_2 NPs] = 4% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 5:5 (*v/v*). **b** Confocal microscopy images of samples that prepared *via* (i) ultrasonication (46 W for 14 s continuously) and (ii) vortex mixing (3,000 rpm for 5 min). [SiO_2 NPs] = 8% *w/w*, [PDMS-NH_2] = 3% *w/w*, water/oil ratio is 5:5 (*v/v*). Inset showing the macroscopic appearance of the emulsions.

#3. (6) Finally, there is the option to simply drop the claim with regards to bridging. I believe the first claim for the facile synthesis of particulate emulsion gels, in particular in combination with the proof-of-concept, is sufficiently strong and diligently investigated to stand fully on its own.

Reply: We thank the referees' positive comments, and believe that we have addressed the question about the bridging claim and have modified some descriptions in our manuscript.

Reviewer #4

"I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts."

Reply: We believe that we have addressed the comments of the three reviewers (see above).

Responses to Reviewers' comments

Reviewer #1

All questions have been addressed clearly and the manuscript has been revised accordingly. The manuscript is recommended for publication in Nature Communications.

Reply: We appreciate the referees' positive comments and support for publication.

Reviewer #2

The manuscript by Wan et al. describes a simple and effective interfacial engineering method that utilizes polymers to precisely program the interfacial assembly of nanoparticles to achieve emulsion gels bridged by a monolayer of surface-sharing nanoparticles. The method avoids the complex steps of emulsification, gelation and surface modification of NPs.The results provide new directions for synthesizing next-generation emulsion gel materials from structured soft templates. After comments were made, the additional experiments related by the authors were carefully performed and clearly expressed. The manuscript is recommended for publication in Nature Communications.

Reply: We greatly appreciate these positive comments and support for publication.

Reviewer #3

After careful review of the authors' replies we find our previously stated scientific concerns sufficiently resolved. The scientific quality of the manuscript warrants publication.

Reply: We greatly appreciate these positive comments.

#3. (1) However, we also note that the quality of writing in the manuscript is only satisfactory. The storyline behind the text is hard to follow, the grammar is incorrect at several instances, and parts of the text contain long lists of numbers. We found the manuscript difficult to read and have the impression that laymen will find it more difficult to comprehend.

Reply: Given that the reviewers did not make the comment "The storyline behind the text is hard to follow" during the initial submission, it was raised after we added the results of our supplemented experiments. Therefore, we re-write these added results and discussions in priority, as well as revise the whole manuscript accordingly. We list three positions (or points), where we do substantial changes to make the story look awesome (we feel), as follows. Here, we highlight the points that we need to revise or re-write in the **Previous version** (second submission) in blue, and highlight the revision language in yellow (we call **New version, i.e., to be submitted version)**. Both versions, including the coherent languages before and after the highlighted that allows to be understood easier, are listed following.

1. **Previous version**: line 25, page 13: "Furthermore, the Gaussian curvature distributions of these emulsion gels in Fig. 2 and Fig. 1c show a sharp peak at $K = 0$ and their asymmetry at the right side, indicating that most of the droplets are planar and the droplet networks' boundaries generate the asymmetry (positive Gaussian curvature)[21], which is direct evidence for the formation of bridged emulsion gels over the presented experimental range (Supplementary

Fig. 14). Additionally, vortexed mixing methods (instead of ultrasonication in our system) yields common emulsions composed of spherical, isolated, and sparse droplets (Supplementary Fig. 15). This is because vortex mixing generates much fewer, larger droplets, such that less droplet collision happens and it will allow the isolate droplets to have enough time to be covered by the polymer–NP assemblies, thus preventing further Ostwald Ripening. This result is also evidence for the formation mechanism of our bridged emulsion gel systems described above. Additionally, we successfully form bridged emulsion gels systems using other functional polymers, as for example amine-terminated polystyrene (PS-NH_2), or changing the oil phase, such as *n*-hexane or tricaprylin (Supplementary Fig. 16), showing their universality.".

New version: line 18, page 8: "If we decreased or increased the concentration of the NPs (C_N, from 2% to 8% *w*/*w*) on the basis of the sample in Fig. 1c, it was found that all samples in these C_N ranges were bridged emulsion gels, and their average droplet diameter (D) decreased from 8.3 ± 2.2 to 2.1 ± 0.8 and 1.5 ± 0.5 μm with increasing C_N (Figs. 1c and 2a, Supplementary Figs. 9 and 10). Such a decrease was derived from the fact that the higher concentration of the NPs can cover more interfaces. Varying C_N did not change the bridged droplets' structure, meaning that the three-phase contact angle was almost kept at ~ 45°. This can be attributed to the simultaneous multiple evolved processes in the formation of bridged droplets, including the attraction of the NPs, the rearrangement of polymer–NP ensembles, and the evolution of droplets (i.e., coalescence of droplets), leading to that the increased numbers of the NPs were recruited by the other polymer chains at the interfaces and thus occupied more interfaces (i.e., smaller droplets). And, along with the droplets' Ostwald Ripening, the tendency of NPs crossing over oil droplets does not change such that the anchoring number of polymers to one NP keeps consistent in forming monolayer bridged structure. Further extreme concentration of the NPs gave rise to the derivation of this three-phase contact angle, as for example at the lower value of C_N (< 1% *w*/*w*) the system formed dispersed emulsions (*vide infra*). This mechanism is also supported by the failure formation of emulsion gels by vortex mixing (Supplementary Fig. 11), due to the inability to bridge large droplets at their slow Ostwald Ripening but fast co-assembly of polymer–NP. If, on the other hand, the C_N was fixed at 4% *w*/*w*, we varied the functional polymer concentration (C_P), from 1% to 10% *w*/*w*.".

Regarding the first position, we reposition the discussion of the results of using vortex mixing to replace the homogenizing to generate emulsions (or emulsion gels), and also polish the language, emphasizing more on the findings. The failure to form emulsion gels using vortex mixing is an auxiliary to demonstrate the formation mechanism of our bridged emulsion gels, where nanoparticles play a critical role in formulating the skeleton of the gels. Therefore, we put these findings following the discussion of the dependence of the variation of nanoparticle concentration on emulsion gel formation and the mechanism thereof.

2. **Previous version**: line 24, page 12: "Varying the mixing ratio of the NP aqueous solution to the oil solution of the polymer when fixing the two components' concentration is another alternative to tailor the morphology of the bridged emulsion gel system. Here, we prepared a series of samples with variations of volume mixing ratio between 4% *w*/*w* NP aqueous solution and toluene solution of 3% *w*/*w* PDMS-NH_2, from 8:2 to 2:8. It was found that the samples prepared from mixing ratios of 8:2–3:7 were NP monolayer structured bridged emulsions with R_D monotonically increasing from 1.3 ± 0.4 to 1.4 ± 0.5 to 1.8 ± 0.8 to 2.1 ± 0.8 to 5.8 ± 1.4 and to 5.9 ± 1.6 μm (Fig. 2d and Supplementary Fig. 13). … Its mechanism may arise from the synergy of two driving forces: its equivalent concentrations in Fig. 2c lie in the edge of the gel zone, giving the ability to form bridged emulsion gel, where a NP monolayer bridged gel would be obtained if the same concentrations are selected with 5:5 mixing; the high volume content of oil phase imparts a strong tendency to phase inversion to w/o type[34]. As such, these two loading forces, somehow, stabilize this gel structure. Furthermore, the Gaussian curvature distributions of these emulsion gels in Fig. 2 and Fig. 1c show a sharp peak at $K = 0$ and their asymmetry at the right side, indicating that most of the droplets are planar and the droplet networks' boundaries generate the asymmetry (positive Gaussian curvature)[21], which is direct evidence for the formation of bridged emulsion gels over the presented experimental range (Supplementary Fig. 14). Additionally, vortexed mixing methods (instead of ultrasonication in our system) yields common emulsions composed of spherical, isolated, and sparse droplets (Supplementary Fig. 15).".

   New version: line 9, page 10: "Varying the mixing ratio of the NP aqueous solution to the oil solution of the polymer when fixing the two components' concentration is another alternative to tailor the morphology of the bridged

emulsion gel system. Here, we prepared a series of samples with variations of volume mixing ratio between 8:2 and 2:8, using 4% *w*/*w* NP aqueous solution and toluene solution of 3% *w*/*w* PDMS-NH_2. It was found that the samples prepared from mixing ratios of 8:2–3:7 were NP monolayer structured bridged emulsions with *D* monotonically increasing from 1.3 ± 0.4 to 5.9 ± 1.6 μm (Fig. 2d and Supplementary Fig. 14). … Its mechanism may arise from the synergy of two driving forces: its equivalent concentrations in Fig. 2c lie in the edge of the gel zone, giving the ability to form bridged emulsion gel, where a NP monolayer bridged gel would be obtained if the same concentrations are selected with 5:5 mixing; the high volume content of oil phase imparts a strong tendency to phase inversion to w/o type[34]. As such, these two loading forces, somehow, stabilize this gel structure. The bridged structures of those emulsion gels are further confirmed by Gaussian curvature distribution analysis (Supplementary Fig. 15). All curves show a sharp peak at $K = 0$ and their asymmetry at the right shoulder (the droplet networks' boundaries generate the positive Gaussian curvature), suggesting that most of the droplets are planar in the boundary shared bridged strucutres[21]. Additionally, we successfully form bridged emulsion gels systems using other functional polymers, as for example amine-terminated polystyrene (PS-NH_2), or changing the oil phase, such as *n*-hexane or tricaprylin (Supplementary Fig. 16), showing their universality.".

For the second position, we reorganize the discussion about Gaussian curvature distribution, demonstrating the boundary-sharing bridge structure of our emulsion gels. The language focuses on the evidence findings, instead of direct data description (the previous version).

3. **Previous version**: line 14, page 20: "Based on the robust encapsulation and storage ability of these emulsion gels, we applied our gels to skin protection, exploiting sunscreen cream as a prototypical model. Here, mimicking the commercial sunscreen cream, anti-sunburn ingredients, including three types of chemical sunscreen active compounds (methylene bis-benzotriazolyl tetramethylbutyl phenol, 8% *w*/*w*, ethylhexyl triazone, 4% *w*/*w*, and bis-ethylhexyloxyphenol methoxyphenyl triazine, 8% *w*/*w*) that can absorb the sun's ultraviolet (UV) rays and two bio-sunscreen ingredients (β-carotene, 0.1% *w*/*w*, and vitamin E, 0.1% *w*/*w*) that enable to scavenge free radicals and lessen UV radiation damage[41], were introduced to the oil phase, where olive oil was selected. The o/w emulsion gels were prepared as the encapsulation experiments (Fig. 4a) used water/oil mixing ratio with 4% *w*/*w* NP and 3% *w*/*w* PDMS-NH_2, and the morphology studies found that the loading of these anti-sunburn compounds did not change the structures of the emulsion gels. In addition, these emulsion gels are non-cytotoxic (Supplementary Fig. 26). Before applying these emulsion gels for skin protection, we first examined their in vitro anti-UV protection ability. Specifically, 50 mg of the samples were applied to the human keratinocyte cell line, to assess their in vitro inhibition behaviors against UV-induced intracellular reactive oxygen species (ROS) generation. Additionally, another four groups, a blank sample, a UV sample, an emulsion sample (which has the same components as the emulsion gels, but was prepared by vortex mixing), and a commercial sunscreen—L'Oreal sample were used for comparison. As shown in Supplementary Fig. 27, UV irradiation dramatically enhanced ROS production in unprotected HaCaT cells. For the emulsion group, the cells also produced a high level of ROS. With the cover of L'Oreal sunscreen, the level of ROS was remarkedly diminished. Most importantly, there was almost no ROS generation in the emulsion gel group (as same as the blank group), which is likely attributed to its excellent UV-shielding performances (Supplementary Fig. 28). It is known that UV-induced ROS could cause oxidative stress and mitochondrial membrane depolarization, leading to apoptosis[42]. As shown in Supplementary Fig. 29, HaCaT cells showed decreased red fluorescence and increased green fluorescence after UV irradiation, indicating the decrease in the mitochondrial membrane potential (ΔΨm) and mitochondrial membrane depolarization. With the cover of emulsion gels, there was almost no mitochondrial membrane depolarization, showing the best protection effects compared to the L'Oreal product and emulsion. After the in vitro experiments, the five groups joined into the in vivo experiments, where 20 mg sample dosage was swabbed evenly to the mouse dorsal with ~ 1 cm^2, and the swabbed skin area was subsequently irradiated by a high-intensity UV spot and the wound site was then recorded. Figure 4b showed the evolution of the irradiated area of one mouse in each group as a function of time. It was found that without any protection, the mouse was heavily burned with a huge wound (the UV group), and the wound got worse on 3rd day, partially healed with time, and left a ~ 0.12 cm^2 scar on 14th day. For the emulsion group, there was still a large area of the burned wound, showing insignificant protection on the skin due to the encapsulated active substances' quickly flowing away. The wound became much smaller if the mouse dorsal was coated with L'Oreal, as for example the wound area decreased from ~ 0.42 to ~ 0.11 cm^2 on 3rd day, showing a certain protection on the skin. Finally, the mouse was not injured by UV spot upon swab coating with the emulsion gels, as appearance as the blank group. This indicates effective resistance to strong UV exposure by the absorption of encapsulated sunscreen ingredients in the

emulsion gels, providing efficient swab coating by excellent viscoelasticity. The relative levels of melanin and erythema for each group further supported these results (Supplementary Fig. 30).".

New version: line 25, page 15: "Based on the robust encapsulation and storage ability of these emulsion gels, we applied our gels to skin protection, exploiting sunscreen cream as a prototypical model. Here, mimicking the commercial sunscreen cream, anti-sunburn ingredients, including three types of chemical sunscreen active compounds (methylene bis-benzotriazolyl tetramethylbutyl phenol, 8% *w*/*w*, ethylhexyl triazone, 4% *w*/*w*, and bis-ethylhexyloxyphenol methoxyphenyl triazine, 8% *w*/*w*) that can absorb the sun's UV rays and two bio-sunscreen ingredients (β-carotene, 0.1% *w*/*w*, and vitamin E, 0.1% *w*/*w*) that enable to scavenge free radicals and lessen UV radiation damage[41], were introduced to the oil phase, where olive oil was selected. The o/w emulsion gels were prepared as the encapsulation experiments (Fig. 4a) used water/oil mixing ratio with 4% *w*/*w* NP and 3% *w*/*w* PDMS-NH_2, and the morphology studies found that the loading of these anti-sunburn compounds did not change the structures of the emulsion gels (Supplementary Fig. 26). In addition, these emulsion gels are non-cytotoxic (Supplementary Fig. 27). Emulsion gel sample aside, an emulsion sample with the same components was prepared by vortex mixing. After these, another three groups, a blank sample, a UV sample (directly UV irradiation), and a commercial sunscreen—L'Oreal sample joined into the in vivo experiments to evaluate their protection ability against UV-induced skin burn, where 20 mg sample dosage was swabbed evenly to the mouse dorsal with ~ 1 cm^2, and the swabbed skin area was subsequently irradiated by a high-intensity UV spot and the wound site was then recorded. Figure 4b showed the evolution of the irradiated area of one mouse in each group as a function of time. It was found that without any protection, the mouse was heavily burned with a huge wound (the UV group), and the wound got worse on 3rd day, partially healed with time, and left a ~ 0.12 cm^2 scar on 14th day. For the emulsion group, there was still a large area of the burned wound, showing insignificant protection on the skin due to the encapsulated active substances' quickly flowing away. The wound became much smaller if the mouse dorsal was coated with L'Oreal, as for example the wound area decreased from ~ 0.42 to ~ 0.11 cm^2 on 3rd day, showing a certain protection on the skin. Finally, the mouse was not injured by UV spot upon swab coating with the emulsion gels, as appearance (Fig. 4b), relative levels of melanin and erythema (Supplementary Fig. 28) were comparable to the blank group, which is consistent with the in vitro results, including their data variation in reactive oxygen species (ROS) generation (Supplementary Fig. 29) and mitochondrial membrane depolarization (Supplementary Fig. 30). This indicates effective resistance to strong UV exposure by the absorption of encapsulated sunscreen ingredients in the emulsion gels (Supplementary Fig. 31) and the jammed interfacial monolayer NPs skeleton, providing efficient swab coating by excellent viscoelasticity.".

For the third position, we re-write the discussions about the in vitro results (including inhibition against intracellular UV-induced ROS generation and mitochondrial membrane depolarization). We put these discussions following the results of skin protection against UV irradiation, to be as supplementary to support such in vivo conclusions. We also polish the languages' coherent context.

In response to the comment "the grammar is incorrect at several instances", we have checked the whole manuscript and corrected the grammar errors as follows:

Line 8, page 12: We have corrected "We note that NP monolayer bridged emulsion gels were also found using large NP (630 nm) with certain range of PDMS-NH_2 concentration" with "We note that NP monolayer bridged emulsion gels were also found using large NP (630 nm) with a certain range of PDMS-NH_2 concentration".

Line 8, page 20: We have corrected "Moreover, β-carotene encapsulated in bridged emulsion gels exhibited superior UV stability (with a retention of 93.7% after 6 h of UV exposure) and thermal stability (with a retention of 95.8% at 70 °C)." with "Based on this, encapsulated β-carotene in bridged emulsion gels had superior resistance to ultraviolet (UV) (with a retention of 93.7% after 6 h of UV exposure) and thermal stability (with a retention of 95.8% at 70 °C)".

Line 25, page 24: We have corrected "We note that the data of the emulsion gel group is better than that of the blank group, this arises from the swab coatability of our viscoelastic emulsion gels and their

effective encapsulation of chemical substances to absorb the UV light, and the bioactive ingredients (β-carotene and vitamin E) may even increase the enzyme activity." with "We note that the data of the emulsion gel group is better than that of the blank group. This arises from the swab coatability of our viscoelastic emulsion gels and their effective encapsulation of chemical substances to absorb the UV light, and the bioactive ingredients (β-carotene and vitamin E) may even increase the enzyme activity.".

Line 22, page 31: We have corrected "Briefly, HaCaT cells were cultured in complete medium solution at 37 °C with 5% CO_2" with "Briefly, HaCaT cells were cultured in a complete medium solution at 37 °C with 5% CO_2".

Line 5, page 33: We have corrected "The melanin and erythema value of the mouse skin were also measured after irradiation" with "The melanin and erythema values of the mouse skin were also measured after irradiation".

In response to the comment "and parts of the text contain long lists of numbers", we simplify long lists of numbers in the manuscript. Below are details about the two versions (highlight rule see above), including the highlighted tedious numbers lists, highlighted simplified descriptions, and the whole paragraph containing themselves. In regard to these numbers, including their complex calculations, we summarize them in Supplementary Fig. 14 and Supplementary Table 1. Here, the significance of these data does not reduce, using two typical samples, i.e., 8:2 and 3:7, to demonstrate the impact of altering the volume mixing ratio upon emulsion gels' morphology.

Previous version: line 24, page 12: "Varying the mixing ratio of the NP aqueous solution to the oil solution of the polymer when fixing the two components' concentration is another alternative to tailor the morphology of the bridged emulsion gel system. Here, we prepared a series of samples with variations of volume mixing ratio between 4% *w*/*w* NP aqueous solution and toluene solution of 3% *w*/*w* PDMS-NH_2, from 8:2 to 2:8. It was found that the samples prepared from mixing ratios of 8:2–3:7 were NP monolayer structured bridged emulsions with R_D monotonically increasing from 1.3 ± 0.4 to 1.4 ± 0.5 to 1.8 ± 0.8 to 2.1 ± 0.8 to 5.8 ± 1.4 and to 5.9 ± 1.6 μm (Fig. 2d and Supplementary Fig. 13). This increase is an indication that the NPs play a key role in determining the emulsion droplet size, since their equivalent concentrations are respective: C_N, 6.4% *w*/*w* (= 4 × 8/5), C_P, 1.2% *w*/*w* (= 3 × 2/5); C_N, 5.6% *w*/*w* (= 4 × 7/5), C_P, 1.8% *w*/*w* (= 3 × 3/5); C_N, 4.8% *w*/*w* (= 4 × 6/5), C_P, 2.4% *w*/*w* (= 3 × 4/5); C_N, 4% *w*/*w* (= 4 × 5/5), C_P, 3% *w*/*w* (= 3 × 5/5); C_N, 3.2% *w*/*w* (= 4 × 4/5), C_P, 3.6% *w*/*w* (= 3 × 6/5); C_N, 2.4% *w*/*w* (= 4 × 3/5), C_P, 4.2% *w*/*w* (= 3 × 7/5), if they are considered by mixing with 5:5. Their equivalent concentrations in Fig. 2c constitute a line with a minus slope that passes the point of sample 2, and locate in gel zone. However, the sample with the mixing ratio at 2:8 showed a completely different morphology, a w/o emulsion gel structure. We note here two points: the first is that it is totally different from the sample in Fig. 2b(ii); its equivalent concentrations in Fig. 2c are 1.6% *w*/*w* (4 × 2/5, C_N) and 4.8% *w*/*w* (3 × 8/5, C_P), both lower than the half of the sample's concentrations in Fig. 2b(ii), but it has a much smaller polygonal emulsion droplet size (4.7 ± 2.0 μm); the second is that it does be a gel, showing a non-flowing character (similar to the inverted vial of sample 2 showed in Fig. 2c)."

New version: "Varying the mixing ratio of the NP aqueous solution to the oil solution of the polymer when fixing the two components' concentration is another alternative to tailor the morphology of the bridged emulsion gel system. Here, we prepared a series of samples with variations of volume mixing ratio between 8:2 and 2:8, using 4% *w*/*w* NP aqueous solution and toluene solution of 3% *w*/*w* PDMS-NH_2. It was found that the samples prepared from mixing ratios of 8:2–3:7 were NP monolayer structured bridged emulsions with *D* monotonically increasing from 1.3 ± 0.4 to 5.9 ± 1.6 μm (Fig. 2d and Supplementary Fig. 14). This increase is an indication that the NPs play a key role in determining the emulsion droplet size, since their equivalent C_N values are decreased from 6.4% to 2.4% *w*/*w*, with the variation of C_P between 1.2% *w*/*w* and 4.2% *w*/*w* (Supplementary Table 1), if they are considered by mixing with 5:5. Their equivalent concentrations in Fig. 2c constitute a line with a minus slope that passes the point of sample 2, and locate in gel zone. However, the sample with the mixing ratio at 2:8 showed a completely different morphology, a w/o emulsion gel structure. We note here two points: the first is that it is totally different from the sample in Fig. 2b(ii); its equivalent concentrations in Fig. 2c are 1.6% *w*/*w* (C_N) and 4.8% *w*/*w* (C_P), both lower than the half of the sample's concentrations in Fig. 2b(ii),

but it has a much smaller polygonal emulsion droplet size (4.7 ± 2.0 μm); the second is that it does be a gel, showing a non-flowing character (similar to the inverted vial of sample 2 showed in Fig. 2c)."

#3. (2) Additionally, at several instances, the text contains very definite interpretations of the data. We recommend to moderate the language by summarizing the evidence found, and stating that this evidence suggests/implies the interpretations provided by the authors.

Reply: We believe we have addressed this issue in the above responses.

Reviewer #4

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reply: We appreciate your co-review of this manuscript.