Supporting Information

Structural Diversity in Cryoaerogel Synthesis

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1. Nanoparticle Characterization

Quasi-spherical platinum nanoparticles

**Figure S1.** UV/Vis spectra (left) and particle size distribution (right) of as-synthesized platinum nanoparticles in aqueous solution. The average diameter is 4.2 nm ± 0.7 nm.

Particle size measurements were acquired with a Zetasizer Nano ZSP from Malvern Panalytical inside of a 3 mL disposable cuvette at room temperature.

UV/Vis absorbance spectra of the platinum nanoparticle solutions were recorded with a Dual-FL (HORIBA Jobin Yvon Inc.) inside of a 3 mL quartz cuvette at room temperature.
2. Effect of Different Freezing Media

Fast Freezing

Figure S2 shows pictures of the as-prepared platinum cryoaerogel coatings that have been discussed in context to figure 2. Here, differences in the network structure are already recognizable with the bare eye. Furthermore, figure S3 presents the results from TEM measurements for the corresponding samples from figure 2. In contrast to the different network structures that can be seen in the SEM images (figure 2), the nanostructure of the underlying building blocks seems to be the same in case of every freezing medium and is consisting of sheet-like structures of directly connected nanoparticles. However, due to the preparation technique for TEM, the measurement might not be representative for the whole sample. Accordingly, maybe only the bigger sheet structures get stuck on the TEM grid, but smaller structures like the dendritic interconnections from figure 2(g-j) get lost during preparation.

Figure S2. Pictures of as-synthesized platinum cryoaerogel coatings freeze-dried after flash-freezing in different media at their respective melting temperature. from left to right: liquid nitrogen (at 77 K), n-hexane, toluene, n-pentane, isopentane (comparable to figure 2 & S3).
Figure S3. TEM images of platinum cryoaerogel coatings freeze-dried after flash-freezing in different media at their respective melting temperature: (a-b) liquid nitrogen (at 77 K), (c-d) n-hexane, (e-f) toluene, (g-h) n-pentane, (i-j) isopentane (comparable to figure 2 & S2).
**Figure S4.** HRTEM images of platinum cryoaerogel coatings freeze-dried after flash-freezing in different media at their respective melting temperature: (a) liquid nitrogen (at 77 K), (b) $n$-hexane, (c) toluene, (d) isopentane (comparable to figure 2, S2 & S3).

**Slow Freezing**

In addition to faster freezing with media (such as $n$-hexane, toluene, $n$-pentane or isopentane) we investigated the effect of very slow freezing. For this, the coatings from Pt nanoparticle solutions were frozen inside of a freezer in cool air atmosphere at 253 K. **Figure S5** displays a picture for the resulting coating material comparable to the SEM & TEM images from figure 3.

**Figure S5.** Photograph of a platinum nanoparticle coating freeze-dried after freezing inside of a freezer at 253 K (in air atmosphere).
3. Influence of Freezing Temperatures

Pictures of platinum cryoaerogel coatings that have been investigated via SEM in figure 4 of the main article are displayed in figure S6. Again, differences in the morphology can already be recognized with the bare eye. Additionally, figure S7 depicts the monolithic, substrate-free cryoaerogels corresponding to figure 5 of the main article.

![Figure S6.](image)

**Figure S6.** Pictures of as-synthesized platinum cryoaerogel coatings freeze-dried after flash-freezing in isopentane at different temperatures. From left to right: 263 K, 223 K, 173 K, 113 K (comparable to figure 4).

![Figure S7.](image)

**Figure S7.** Pictures of self-supporting platinum cryoaerogels freeze-dried after flash-freezing in isopentane at different temperatures. From left to right: 263 K, 223 K, 173 K, 113 K (comparable to figure 5).
4. Improvements by Longer Freezing Periods

**Storing in the frozen state at 77 K**

While figure 6 only shows a selection of SEM images for different freezing periods, figure **S9** shows the complete series of investigated samples. In addition to that, figure **S8** shows photographs of the corresponding cryoaerogel coatings. As explained, with prolonged freezing duration, over the first hours, a continuous improvement of the film was observed regarding covering and homogeneity. Maximum improvement was achieved after 24 h in the frozen state. Longer freezing periods caused no further improvement, but the same (highest) quality.

![Figure S8. Pictures of platinum cryoaerogel coatings frozen with liquid nitrogen and stored (in the frozen state) at 77 K for different times before freeze-drying. From left to right: 10 minutes, 1 hour, 3 hours, 6 hours, 24 hours, 48 hours, 72 hours (comparable to figure S7).](image)
Figure S9. SEM images of platinum cryoaerogel coatings frozen with liquid nitrogen and freeze-dried after different times in the frozen state: (a) 10 minutes, (b) 1 hour, (c) 3 hours, (d) 6 hours, e) 24 hours, f) 48 hours, (g) 72 hours.

**Stability in Wet Chemical Environment**

With regard to potential applications, the stability of platinum cryoaerogel coatings was tested in wet chemical environment. For this reason, the as-prepared cryoaerogel coatings were submerged in water for 30 minutes at room temperature, then taken out and dried under ambient conditions. Afterwards, the remaining amount of platinum on the substrate was detected via ICP-OES. Corresponding results can be found in figure S10.

Until now, noble metal aerogel coatings were not sufficiently stable against water treatment without the use of any binding additive. Forces such as surface tension, adhesion or thermal convection lead to a partial or even complete collapse of the network and their detachment into the solution. In this work, however, it can be seen, that the stability of additive-free cryoaerogel
coatings is even improved in wet chemical environment, when stored in the frozen state before freeze-drying. Thus, compared to the standard procedure (where the freezing period is 10 min) we were able to enhance the stability of coatings from noble metal aerogels and at the same time avoid the addition of any binding material.

![Graph](image)

**Figure S10.** Platinum amounts of cryoaerogel coatings frozen in liquid nitrogen and kept in the frozen state at 253 K for different times before freeze-drying and submerged in water for 30 minutes afterwards. Determined with ICP-OES and related to the initially applied amount of Pt.

**Storing in the frozen state at 253 K**

Beyond freezing and storing the samples in liquid nitrogen at 77 K, the improvement of covering, homogeneity and stability is also evident when samples are stored at other temperatures below their melting point (~273 K). In this context, **figure S11 and S12** demonstrate the pictures and morphologies for platinum cryoaerogel coatings that have been frozen with liquid nitrogen at 77 K, but stored in a freezer at 253 K. Here, the same trend is apparent: with prolonged freezing duration, over the first hours, a continuous improvement of covering and homogeneity can be observed. Maximum improvement is achieved after about 24 h in the frozen state and longer freezing periods cause no further improvement, but the same (highest) quality.
Accompanying with the results for storage at 77 K, the very same trend is apparent regarding the mechanical stability of the coating. In this context, figure S13 shows the results from ICP-OES measurements regarding the remaining platinum amount of the as-prepared coatings related to the initially applied Pt amount.

**Figure S11.** Pictures of platinum cryoaerogel coatings frozen with liquid nitrogen and stored (in the frozen state) at 253 K for different times before freeze-drying. From left to right: 10 minutes, 3 hours, 24 hours, 72 hours (comparable to figure S10).

**Figure S12.** SEM images of platinum cryoaerogel coatings frozen with liquid nitrogen and stored (in the frozen state) at 253 K for different times before freeze-drying: (a) 0 hours (freeze-dried immediately after freezing), (b) 3 hours, (c) 24 hours, (d) 72 hours.
Figure S13. Platinum amounts of cryoaerogel coatings frozen in liquid nitrogen and kept in the frozen state at 253 K for different times before freeze-drying. Determined with ICP-OES and related to the initially applied amount of Pt.
5. Specific Surface Area Measurements

Nitrogen physisorption measurements have been carried out to investigate the specific surface area of platinum cryoaerogels prepared with different freezing media.

Initially, cryoaerogel coatings were produced, but they did not lead to any evaluable results during the measurement. Due to the limited space and the geometry of the samples, for a representative measurement not enough sample material could be introduced into the measuring device (at least 30 mg are necessary). Even changing the adsorbed gas (nitrogen, argon, xenon) did not lead to success at this point.

Therefore, BET measurements could only be performed with more voluminous, substrate-free, cryoaerogels, which, on the other hand, are probably not representative for the investigated coatings from the main manuscript. However, for the measurements we prepared voluminous, substrate-free gels (~35 mg) by freezing either in liquid nitrogen at 77 K (our standard procedure) or in isopentane at 113 K. Measurements were carried out on a Nova 3200e Surface Area & Pore Size Analyzer from Quantachrome Instruments. The outgas time was 30 min. at a temperature of 20°C Specific surface areas were determined from the adsorption isotherms using the Brunauer-Emmett-Teller (BET) method. Resulting adsorption isotherms of the cryoaerogels are displayed in figure S14 and exhibit IUPAC type IV behavior of monolayer-multilayer adsorption. In agreement with the morphologies derived from SEM measurements, the subsequent hysteresis loop is attributed to capillary condensation within the pore system in the material. Further, specific surface areas have been estimated via the multipoint-BET method and were about 43 m² g⁻¹ for freezing in liq. nitrogen and 39 m² g⁻¹ for freezing in isopentane respectively. In comparison to the maximum achievable surface area for single platinum nanoparticles (which is about 62 m² g⁻¹ for Pt nanoparticles with an average diameter of 4.2 nm), both superstructures show a similar large surface area indicating nearly complete accessibility of the possible surface area.
However, these results did not show the expected trend that faster frozen cryoaerogels offer a higher specific surface area. In this context, we strongly suppose that cryoaerogels with more voluminous macroscopic shapes behave differently and cannot be compared to thin films. Additional to the similar surface areas we further observed similar pore size distributions in figure S15. These results suggest that in case of the voluminous, substrate-free cryoaerogels nearly the same network structure was formed for both samples frozen with different media. We suppose, that in these cases the higher volume of the sample leads to a decrease of the freezing speed within the sample. Since we show that the freezing speed has a direct influence on the crystallization and network structure that is formed, we suspect that a cell-like structure may no longer be formed when voluminous samples were frozen with isopentane, but rather a structure comparable to slower frozen samples (with liq. nitrogen). This suspicion is supported by the corresponding SEM images (figure 6g-h) from voluminous cryoaerogels frozen with isopentane, which do not show a clear cell-like, but a more randomly arranged network of sheet-like segments similar to those of voluminous gels frozen with liquid nitrogen. As we already mentioned, therefore it can be assumed, that voluminous cryoaerogels differ in their (structural) properties from thin films and the physisorption measurements are not representative for the thin film materials discussed in the main paper.

Though, in another article, which was accepted recently, we investigated the surface areas of thin cryoaerogel films in a better suited way by means of electrochemical measurements.[1] There, noticeably different electrochemically active surface areas (ECSAs) were observed for the different network structures. We further applied these materials for the first time to an electrocatalytic application and showed that the catalytic activity of these materials can be increased by the control over the network structure.
Figure S14. Nitrogen physisorption isotherms for substrate-free platinum cryoaerogels. Left: frozen with liquid nitrogen at 77 K (standard procedure), Right: frozen with isopentane at 113 K. Black lines denote adsorption, red lines denote desorption.

Figure S15. Pore size distributions for substrate-free platinum cryoaerogels. Left: frozen with liquid nitrogen at 77 K (standard procedure), Right: frozen with isopentane at 113 K.

6. References

[1] D. Müller, D. Zámbó, D. Dorfs, N. C. Bigall, Cryoaerogels and Cryohydrogels as Efficient Electrocatalysts, Small, 2021, accepted.