Versatile fabrication method for aerogels by freezing and subsequent freeze-drying of colloidal nanoparticle solutions

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Abstract:

We present a novel approach for synthesizing aerogels by shock-freezing colloidal nanoparticle in liquid nitrogen and subsequent freeze drying. With this simple method it is possible to assemble nanoparticle into macroscopic voluminous monoliths, while retaining most of their properties such as size, shape or optical properties. In comparison to state of the art techniques it is a lot faster and easier to handle. This procedure might bridge the gap for scaled-up production and might enable industrial applications.

Introduction:

In 1931 Kistler et. al. reported on a new route to dry jellies of silica or alumina by supercritical drying, resulting in a complete new group of materials: the aerogels.[1] These materials were basically made out of air (>99%) but still showed mechanical stability. In 2005 the group around Brock reported on the possibility to build these Aerogels out of colloidal NP building blocks enabling to preserve the nanoparticle properties outside of their liquid medium.[2] Since then a lot of reports focused on Aerogels with interesting properties such as plasmonic or photoluminescent features or high specific surface areas.[3-5] However one major drawback is the complex, long and expensive fabrication of the gels which we overcome with the here presented method.

Results and discussion:

We discovered that by concentrating aqueous nanoparticle colloids up to a certain threshold (which is a volume fraction of nanoparticle higher than 0.1%), shock freezing in liquid nitrogen and subsequent freeze drying an aerogel-like superstructure can be obtained (see figure 1).

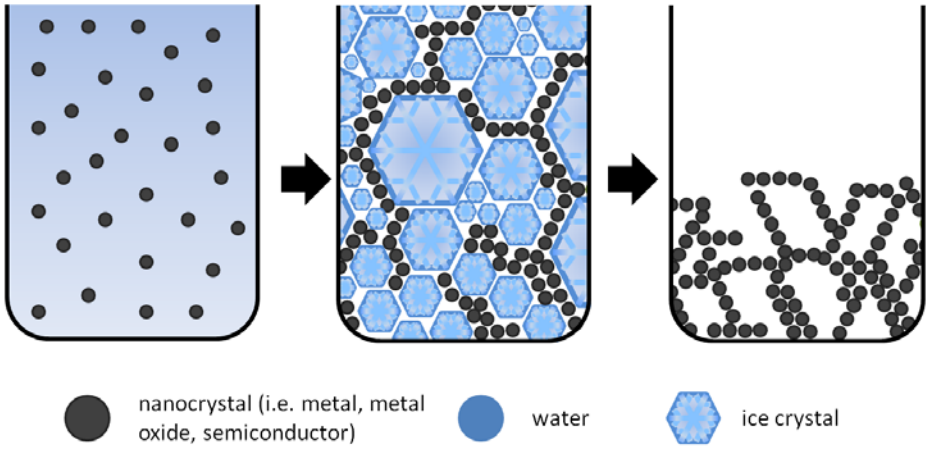

Figure 1: Scheme of the freezing process of colloidal nanoparticle with subsequent freeze drying

In our work we were able to show highly porous and voluminous monoliths (see figure 2) out of (noble) metals (e.g gold, silver, palladium, platinum), semiconductors (CdSe/CdS) as well as metal oxides (hematite) with densities ranging from 20 to 60 mg cm^{-3} (corresponding to a relative density of around 0.2%). The monoliths consist of the nanoparticle building blocks assembled in thin sheets or wires (which we assume as enrolled sheets). These sheets and wires again are crosslinked with each other, building the framework of the monoliths (see figure 3). The sheets exhibit a roughness on the nanometer scale and also high specific surface areas (which could be determined e.g. platinum monoliths with 33m^2g^{-1}) in the magnitude of comparable aerogels.

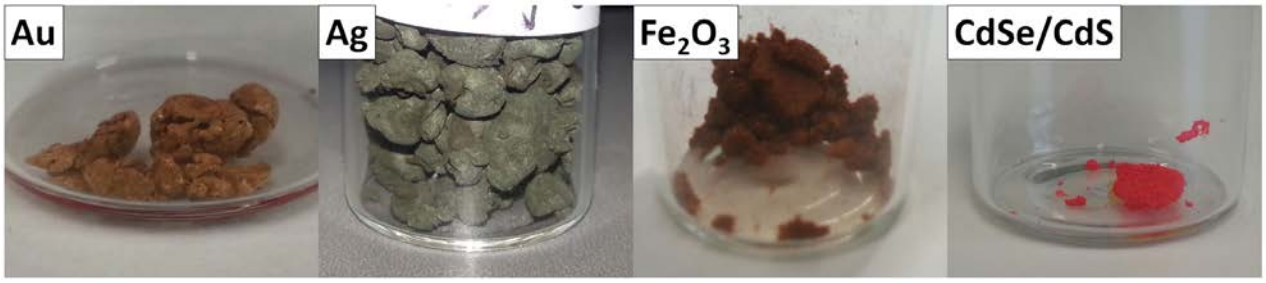

Figure 2: Monoliths of gold, silver, hematite and CdSe/CdS (top)

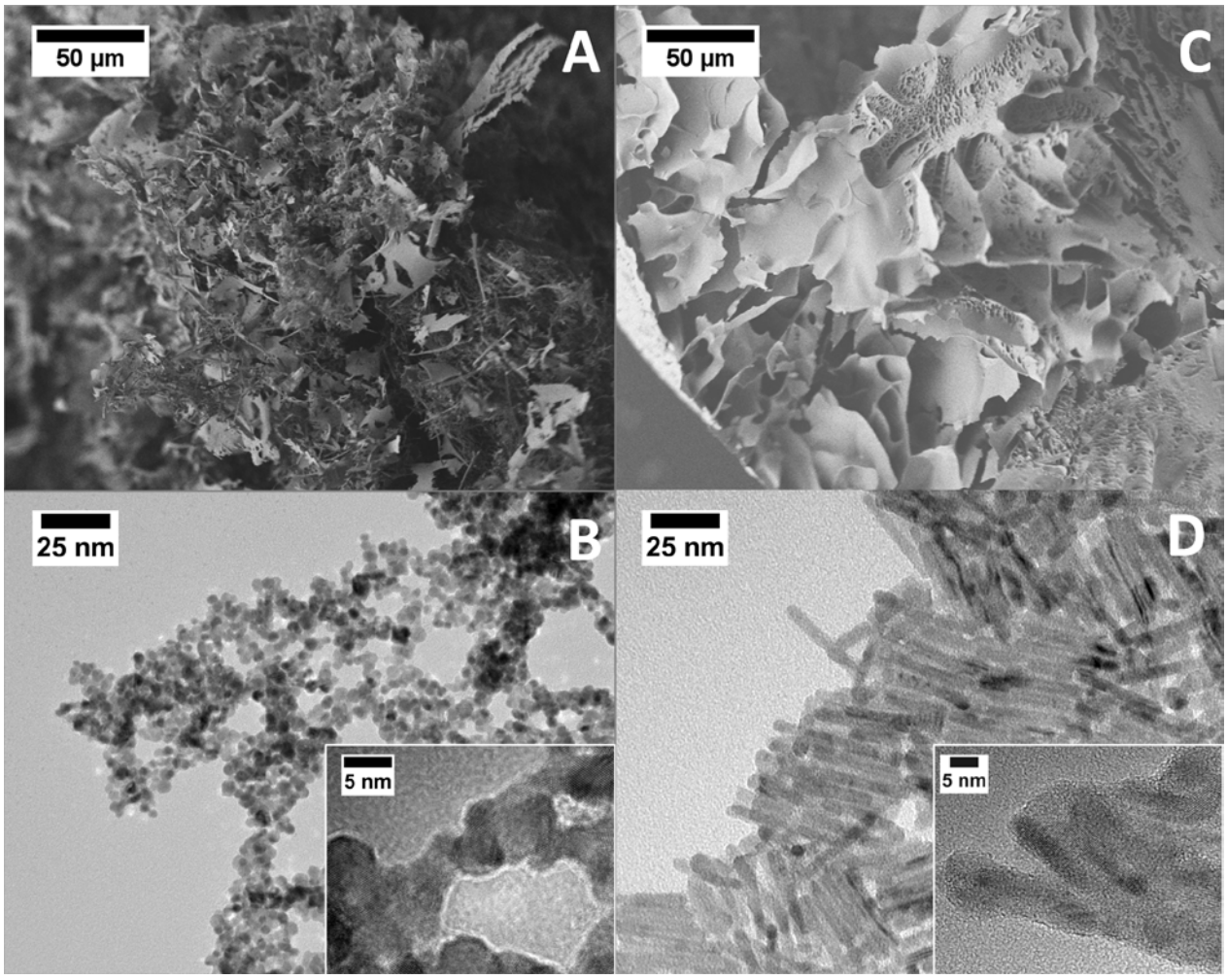

Figure 3: SEM/TEM characterization of palladium nanospheres (A-B) and CdSe/CdS nanorods (C-D) assembled into aerogels

Beside the mostly similar properties of the resulting aerogels to conventional ones, our method has significant advantages. Since this method is solely depended on physical properties, any material and shape can be processed into aerogels (as long as the building blocks are in an aqueous solution), and so far every tested nanomaterial could successfully be assembled to aero-

gels by this route. Furthermore, we can achieve sophisticated geometries by means of molding, as well as homogenous aerogel films on different substrates (see figure 4) with thicknesses of 10 – 50 µm.

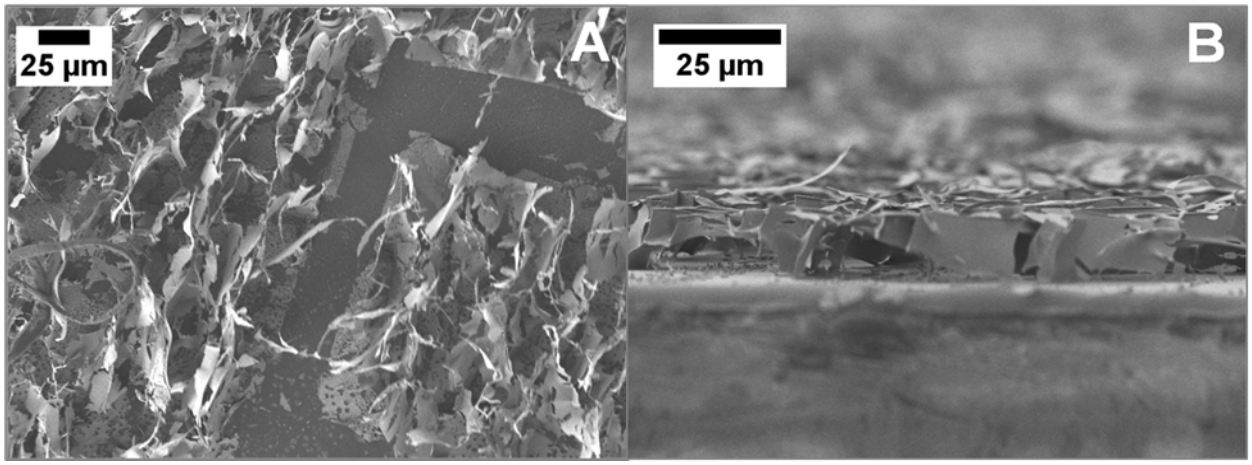

Figure 4: Top view (A) and cross section (B) of Pd aerogel film on glass substrate

The possibility of making various shapes and sizes of the aerogels might bridge the gap from laboratory to industry enabling for example catalyst-designing. The results of this work and further details were published in Angewandte Chemie.[6]

Conclusion:

In this work we fabricated monolithic aerogels out of nanoparticles of gold, silver, platinum, palladium, cadmium selenide/cadmium sulfide and hematite as various shaped monoliths including thin films and more sophisticated geometries (e.g. smoking smiley). Characterizations showed the preservation of the nanoparticle building blocks, specific surfaces areas comparable to literature and first catalytic measurements showed activity for heterogenous gas phase reaction (e.g. CO-conversion) and photocatalytic reactions.

Acknowledgements:

N.C.B., A.F., S.S.-P., S.N., and J.P. are grateful for financial support from the German Federal Ministry of Education and Research (BMBF) within the framework of NanoMatFutur, support code 03X5525. I.K. and D.W.B. gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG, SPP1613).We also would like to thank Dr. Dirk Dorfs and Dominik Hinrichs for scientific discussions.

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